



1982

## Chemical Activation By Low Energy Electron Impact Of Carbon Monoxide Adsorbed On Metal Surfaces (Gold, Nickel, Palladium, Molybdenum, Tungsten)

James Dean White  
*University of the Pacific*

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CHEMICAL ACTIVATION BY LOW ENERGY  
ELECTRON IMPACT OF CARBON MONOXIDE  
ADSORBED ON METAL SURFACES

---

A Dissertation  
Presented to  
the Graduate Faculty of  
the University of the Pacific

---

In Partial Fulfillment  
of the Requirements for the Degree  
Doctor of Philosophy

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by  
James Dean White

July, 1982

This dissertation, written and submitted by

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Dated July 30, 1982

## DEDICATION

This is dedicated to my wife, Kathy, who was with me every step of the way and who shared the vision.

---

## ACKNOWLEDGMENTS

Trust in the Lord with all your heart, and do not lean on your own understanding. In all your ways acknowledge Him, and He will make your paths straight.

Proverbs 3: 5,6 (NAS)

I also wish to express my appreciation to Dr. Patrick Jones who served not only as my research advisor, but also as an occasional glass blower, spot welder and solace through the many ups and downs of putting this together.

Thanks also go to my mother, Irene, and my wife's mother, Mary, who have been supportive of this effort in countless ways which have not gone unnoticed.

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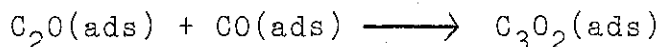
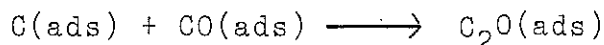
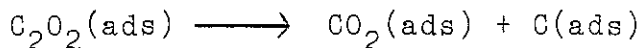
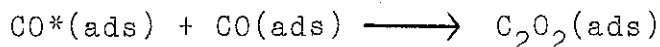
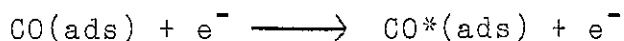
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## ABSTRACT

A technique has been developed for determining the effect of very low energy electrons (3.0 to 8.0 eV) on molecules adsorbed on metal surfaces. The electron source is a thorium coated iridium filament operated at low filament current to minimize the thermal distribution of the energies of emitted electrons (0.0 to 0.4 eV). The system is kept at  $10^{-3}$  to  $10^{-4}$  torr by allowing the gas studied to pass through the reaction vessel while the system is being evacuated by Vac Ion pumps. Analysis is performed via computer controlled quadrupole mass spectrometry.

Carbon monoxide gas has been studied on gold, nickel, palladium, molybdenum and tungsten surfaces produced by vacuum sublimation of the metals. Observations fit the following series of reactions:



Since desorption occurs along with these reactions, the mass levels of 44 ( $\text{CO}_2$ ), 56 ( $\text{C}_2\text{O}_2$ ) and 68 ( $\text{C}_3\text{O}_2$ ) were monitored as a function of electron energy. Threshold potentials (ie. the potential at which the mass spectrometer ion current

begins to increase for a given mass level) were determined for the surfaces studied. Good agreement has been obtained for the threshold potentials ( $E_{th}$ ) determined at the three mass levels for a given metal surface. Average values are:  $E_{th}(\text{gold}) = 6.0 \text{ eV}$ ;  $E_{th}(\text{nickel}) = 6.1 \text{ eV}$ ;  $E_{th}(\text{palladium}) = 4.8 \text{ eV}$ ;  $E_{th}(\text{molybdenum}) = 4.1 \text{ eV}$ ;  $E_{th}(\text{tungsten}) = 3.0 \text{ eV}$ .

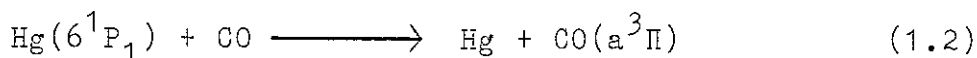
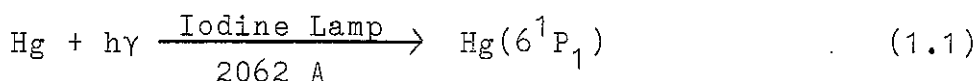
A relationship between these threshold potentials and the heats of adsorption for CO adsorbed on the surfaces studied has been proposed. The heat of adsorption is believed to be primarily a function of  $d\pi \rightarrow p\pi^*$  back bonding from the metal to the surface bound carbonyl. This stabilizes the  $\pi^*$  orbital relative to the gas phase and lowers the excitation energy of CO by the heat of adsorption.

## Chapter 1

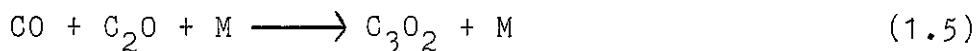
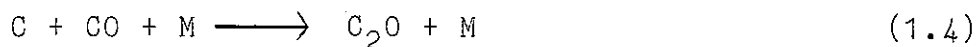
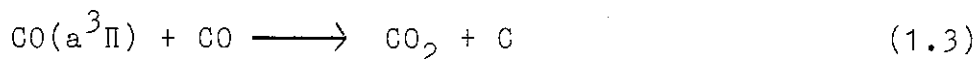
### Introduction

Low energy electron impact has been proven to be a useful tool in the elucidation of electronic and vibrational structure in gas phase molecules.<sup>1</sup> It is unique relative to photon impact in that it can promote electronic transitions which are optically forbidden. The cross sections for these transitions are often high ( $>1 \times 10^{-17} \text{ cm}^2$ ).<sup>2</sup>

It would appear that low energy electron impact may be a useful tool for the production of metastable excited state molecules whose subsequent reactivity could then be studied. Other methods suffer from the presence of added impurities which may themselves serve as reaction sites. For example,  $\text{CO}(a^3\Pi)$  has been produced as follows:<sup>3</sup>



It is then believed to enter into the following series of reactions:





Step 1.3 is a disproportionation reaction which is known to occur also on metal surfaces. Although efforts were made in the study cited to scavenge the residual mercury, the potential interaction of CO with mercury or mercury oxide cannot be ruled out.  $\text{CO}(a^3\Pi)$  cannot be produced directly by photon impact since this involves an optically forbidden transition. Appendix F describes some of the work done in this lab to develop a technique for chemical activation of gas phase molecules by low energy electron impact.

The main reason the gas phase electron impact work did not lead to meaningful results was that a high electron beam current ( $>0.01$  mA) at relatively high pressure ( $>0.1$  torr) was needed to produce sufficient products for analysis. High pressures are very destructive to sources of high electron current. This suggests that if molecules can be concentrated in a region isolated from the electron source, low energy electrons could be used to induce electronic transitions and subsequent chemical reactions. Such a situation exists when gases are adsorbed on a metal surface. The concentration of molecules at the surface is high and the electron source can be operated under vacuum.

Low energy electron diffraction (LEED) has been used to study the structure of molecules adsorbed on metal surfaces.<sup>4</sup> Auger electron spectroscopy (AES) has been used to determine the electronic energy levels of these systems.<sup>5</sup> Electron energy loss spectroscopy (EELS) has been used to determine vibrational fine structure of adsorbed molecules.<sup>6</sup>

However, comparatively little has been done to study the chemical reaction(s) which are induced at the surface as a result of low energy electron impact on surfaces. The fundamental problem is that a method has not existed in which a sufficiently monoenergetic electron beam could be produced at less than 15 eV at sufficient intensity.

Menzel has pointed out the problems which exist even in studying the effect of electron impact at higher electron energies.<sup>7</sup> One has a choice of analyzing the products produced (say by mass spectrometry) or studying the residual products on the surface with a suitable method (such as LEED). The necessity of producing monoenergetic electrons at relatively high current imposes severe problems on the former choice. However, work has been done at relatively high energies (80 eV) where the electron current is high. The latter method has been used extensively.<sup>8</sup>

It would be extremely desirable to produce low energy electrons (3.0 to 8.0 eV) at relatively high current (>0.01 mA) and identify the products produced as a result of their interaction with molecules adsorbed on the surface of metals. With such a method it would be possible to determine the energy threshold at which a reaction occurs if a suitable method could be found with which to monitor the concentration of the products.

This report demonstrates that such a method has been developed by going to a radically simple design. The electron source is a thorium coated iridium filament. These

filaments are unique in that they are stable in a wide variety of environments and operate at relatively low temperatures (600 to 1000 °C). The filament is exposed to pressures as high as  $10^{-3}$  torr in our system and no attempt was made to provide electron optics. This was not necessary because the filament current used was so low that the emitted electrons have a very small distribution of energies (0.0 to 0.4 eV). The low operation temperature resulted in very little radiant energy reaching the collector where the electron impact phenomena was taking place.

Carbon monoxide adsorbed on gold, nickel, palladium, molybdenum and tungsten surfaces was studied in this way. Products were followed via mass spectrometry. It has been reported that when mercury light is shined on a tungsten surface which has been exposed to carbon monoxide, the products observed are  $\text{CO}_2$ ,  $\text{C}_2\text{O}$ ,  $\text{C}_2\text{O}_2$  and  $\text{C}_3\text{O}_2$ .<sup>9</sup>  $\text{C}_3\text{O}_2$  has also been observed in this laboratory when UV light is directed at carbon monoxide adsorbed on a palladium surface. Because of these observations, and because of the products observed in the gas phase, mass levels 44 ( $\text{CO}_2$ ), 56 ( $\text{C}_2\text{O}_2$ ) and 68 ( $\text{C}_3\text{O}_2$ ) were followed during the threshold excitation studies. It was not possible to follow mass level 40 ( $\text{C}_2\text{O}$ ) during a threshold study because of the small change observed and the high residual pressure of argon common to mass spectrometer systems.

## Chapter 2

### Experimental

#### 2.1 Reagents

All reagents were used as received without further purification. The following reagents were obtained from Alfa Products; palladium wire (99.9%, 0.25 mm diameter), nickel wire (99.99%, 0.25 mm diameter), gold wire (99.99%, 0.127 mm diameter), tungsten wire (99.98%, 0.25 mm diameter) and molybdenum hexacarbonyl (98%).

Carbon monoxide gas (Linde, CP grade) was used for the bulk of the studies. The mass spectrum from 2 to 50 amu showed no detectable impurities. Oxygen (Linde) and hydrogen (Linde) gases were used as received in 3500 psig cylinders.

#### 2.2 Equipment

Mass analysis was done with a Varian CVA-5 mass spectrometer which was designed around a Uthe Technology, Incorporated (UTI) 100B quadrupole mass analyzer. The mass level was controlled externally with a S-100 based microprocessor from Godbout Electronics. The microprocessor also collected the ion current data and processed it. Details of the mass spectrometer/microprocessor interface hardware are provided in Appendix A. Software developed for control, data collection, data reduction and data output

is described in Appendixes B through E.

Figure 2.2.1 illustrates the flow system for introducing the gas(es) into the reaction vessel and then into the mass spectrometer for analysis. In this series of experiments, only one gas inlet was used. All elbows, tees and tubing were stainless steel and all joints were silver soldered. A typical gas cylinder for attachment to the gas inlet is shown in Figure 2.2.2 drawn to scale. The Varian Vac Ion pump (Type 911-5021) was attached to reduce the background spectrum to a minimum and to reduce the pressure in the reaction chamber.

A detailed diagram of the reaction vessel is shown in Figure 2.2.3 drawn to scale. It was assembled from a Huntington VF-070 stainless steel cross (flange O.D. = 0.75", tube O.D. = 1.33", copper gaskets), a Huntington IF-053 8 wire feedthrough (with matching flanges), two Huntington 133-025R Vac-U-Flat flanges (I.D. = 0.26", for connection of the  $\frac{1}{4}$ " stainless steel tubing to the gas inlet and outlet) and one Huntington 133-075R flange (I.D. = 0.63", for connection to the vacuum gauge tube).

The vacuum gauge tube was only in place when calibrating the pressure reading available from the mass spectrometer's total pressure function. At all other times, a Huntington 133-000T mini blank flange was in place. The additional volume has a dampening effect on the change in intensity at a mass level if the vacuum gauge tube is left in place.

Figure 2.2.1

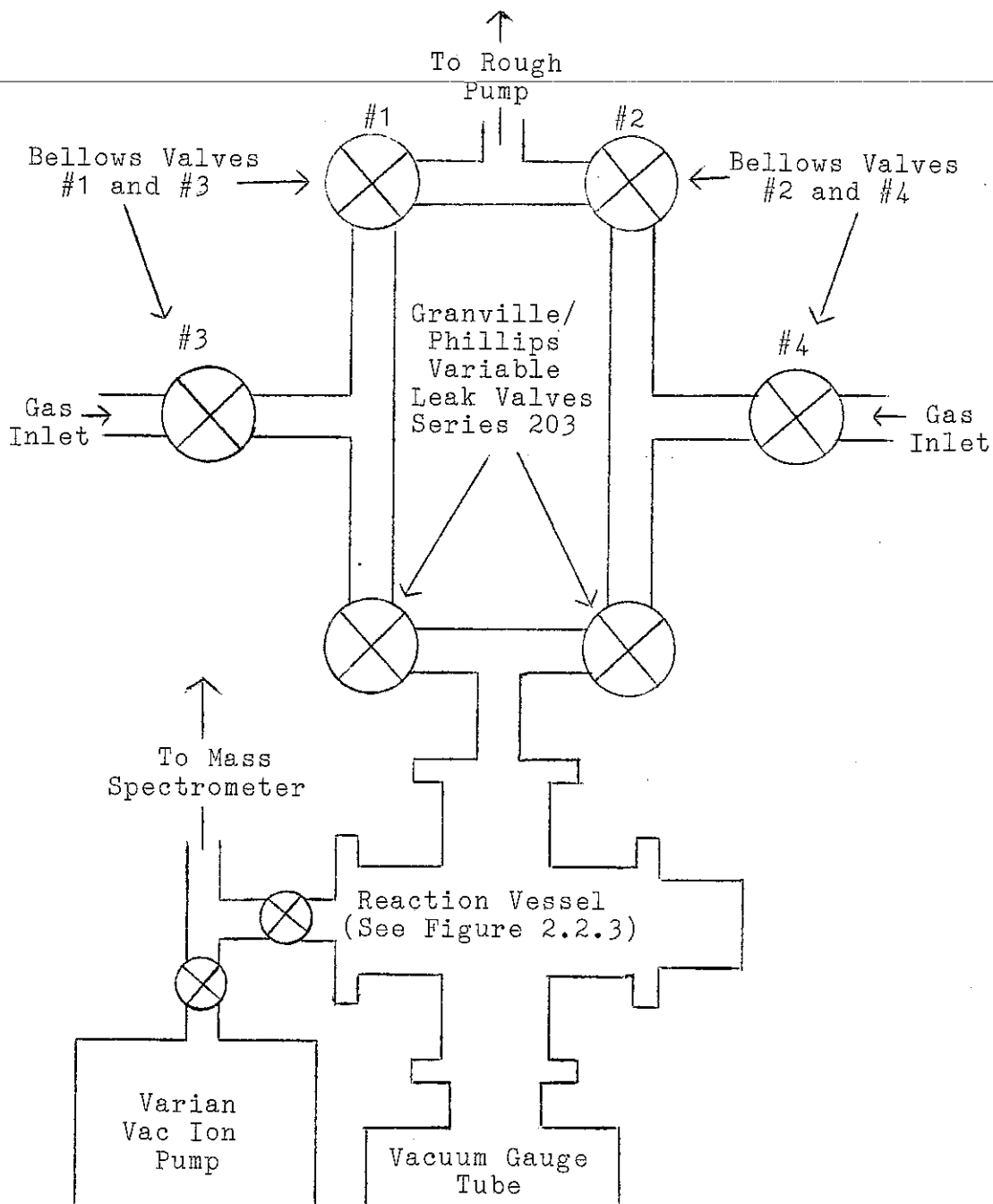
Flow System for Introducing  
Gas in the Reaction Vessel

Figure 2.2.2

Typical Gas Cylinder for  
Introduction of Gases  
Drawn to Scale

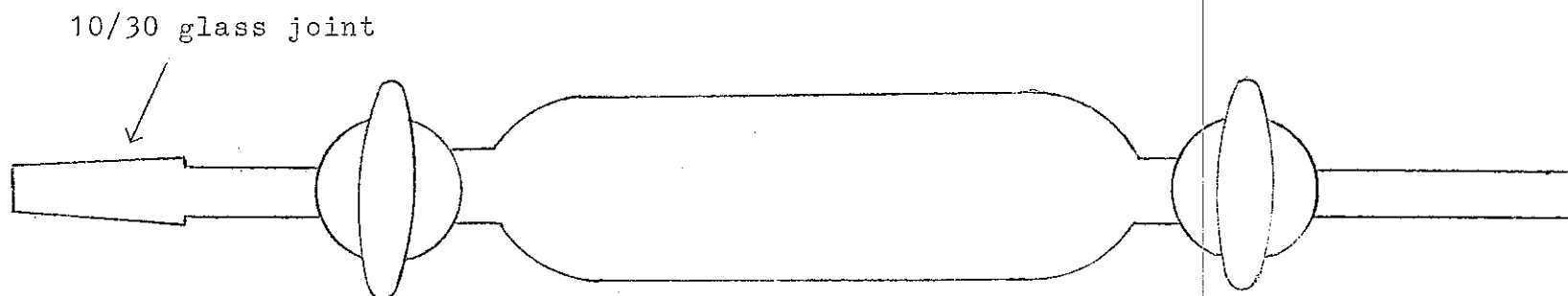
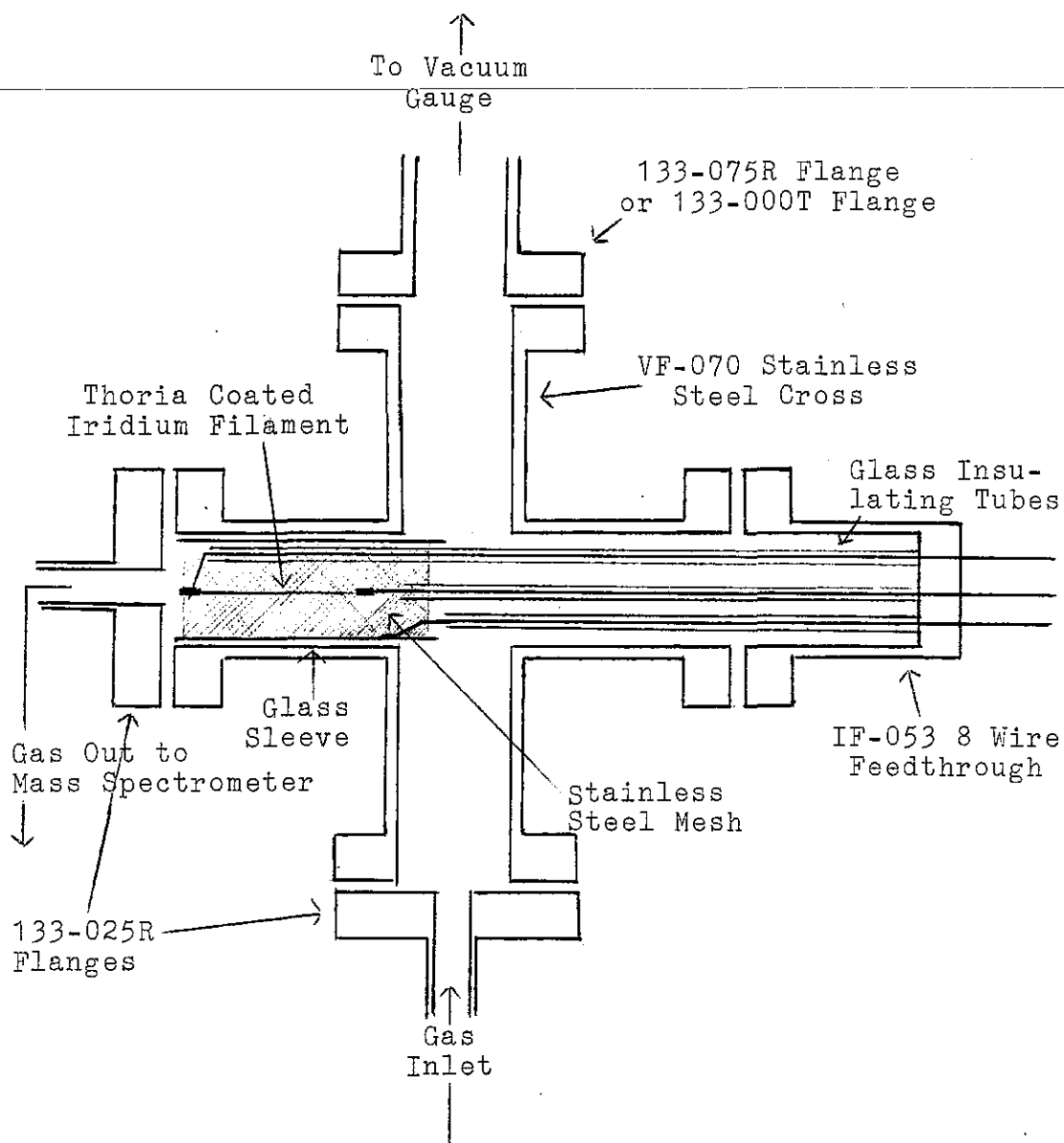


Figure 2.2.3

Reaction Vessel  
Drawn to Scale

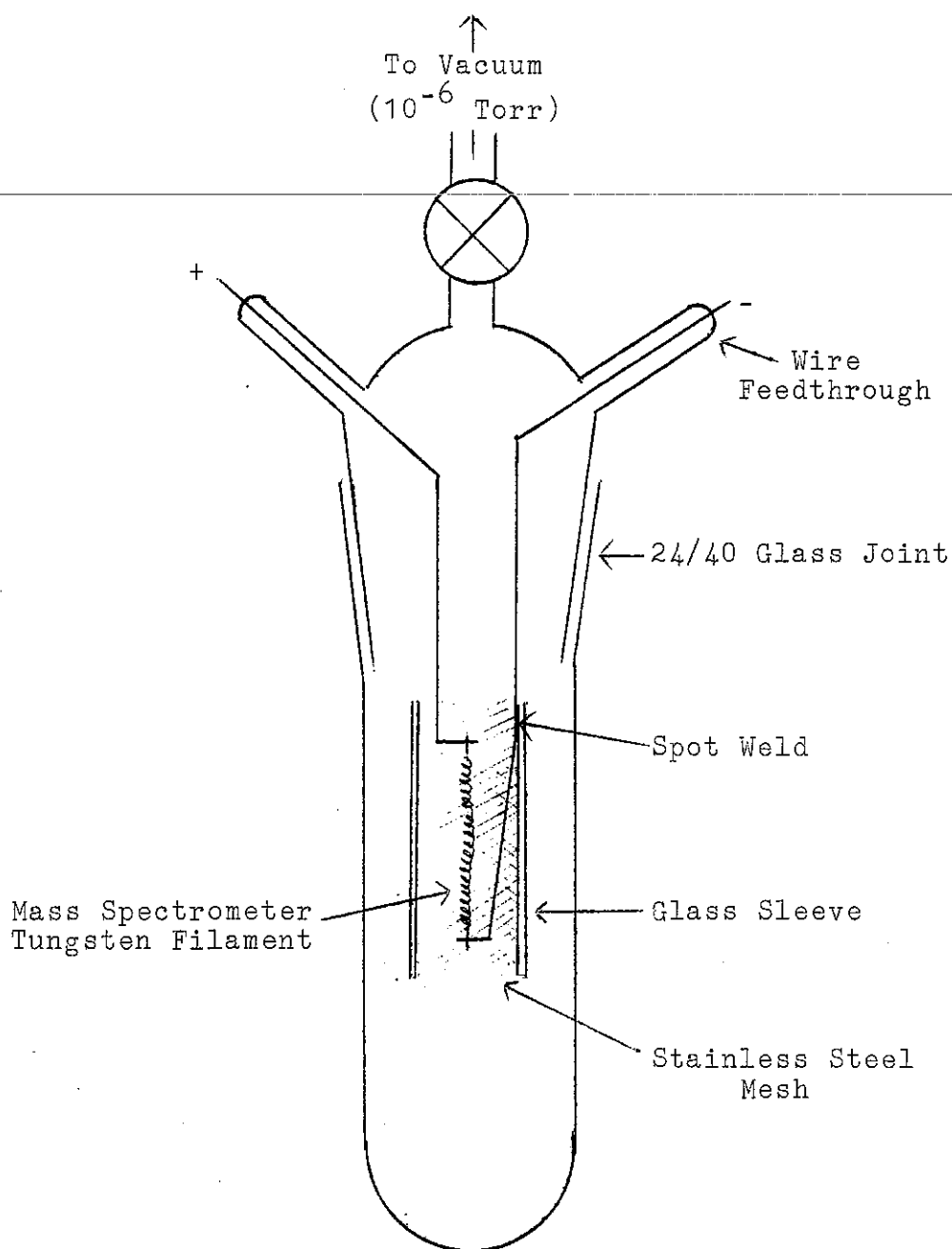


A 1.0 cm thoria coated iridium filament from Electron Technology, Incorporated is spot welded to two of the wire feedthroughs approximately in the center of the tube. Surrounding this is a 3.8 cm long 100 mesh stainless steel tube with a pyrex sleeve for insulation. The stainless steel tube is spot welded to a third wire feedthrough and the other wire feedthroughs are cut short.

~~The stainless steel mesh and pyrex tube were coated~~ with the metal of interest (palladium, gold, nickel, tungsten or molybdenum) in the apparatus shown in Figure 2.2.4. A separate mesh and sleeve was used for each metal. For palladium and gold, the wire of interest was wrapped around the tungsten filament. The stainless steel tube, with its pyrex sleeve, was then spot welded into place and the system was pumped down to approximately  $1 \times 10^{-6}$  torr. At this point current was passed through the tungsten filament until the metal began to sublime and an opaque film of the metal coated the stainless steel tube and pyrex sleeve. Care was taken to stay well below the sublimation temperature of tungsten.

In the cases of nickel and tungsten, the filament was replaced with a 0.25 mm diameter strand of the wire of interest, and current was passed through the wire until an opaque film resulted. For nickel, it was necessary to wrap two wires together. In all cases, the opaque part of the film was 1.5 to 2.0 cm long. When mounting the assembly within the reaction vessel, great care was taken to position

Figure 2.2.4

Assembly for Generating  
Thin Metal Films

the iridium filament in the center of the metal coated cylindrical collector.

A coating of molybdenum was obtained by placing 0.5 to 1.0 g of molybdenum hexacarbonyl in the bottom of the tube. A strand of 0.25 mm diameter tungsten wire formed the filament. The vessel was pumped down until the pressure remained constant and the molybdenum hexacarbonyl had several minutes to sublime. Current was then passed through the tungsten filament to bring it to a red heat (well below the sublimation temperature of tungsten). An opaque film of molybdenum was obtained after about two hours.

Electrical connections to the reaction vessel are shown in Figure 2.2.5. Filament current was supplied by a Hewlett-Packard Model 6284A regulated power supply and was monitored with a Simpson Model 464 digital multimeter. The potential between the filament and collector was set with a Hewlett-Packard Model 6204B regulated DC power supply which was monitored with a Keithley Model 169 digital multimeter. Another model 169 was used to read emission current (current passing from the filament to the collector) during thermionic emission of electrons.

A Veeco Type RG31-X vacuum gauge with a Bayard-Alpert type vacuum gauge tube (NRC Model 571-SK) was used to read pressure in the reaction vessel when calibrating the mass spectrometer's total pressure function scale.



## 2.3 Procedures

### 2.3.1 Pressure Determinations

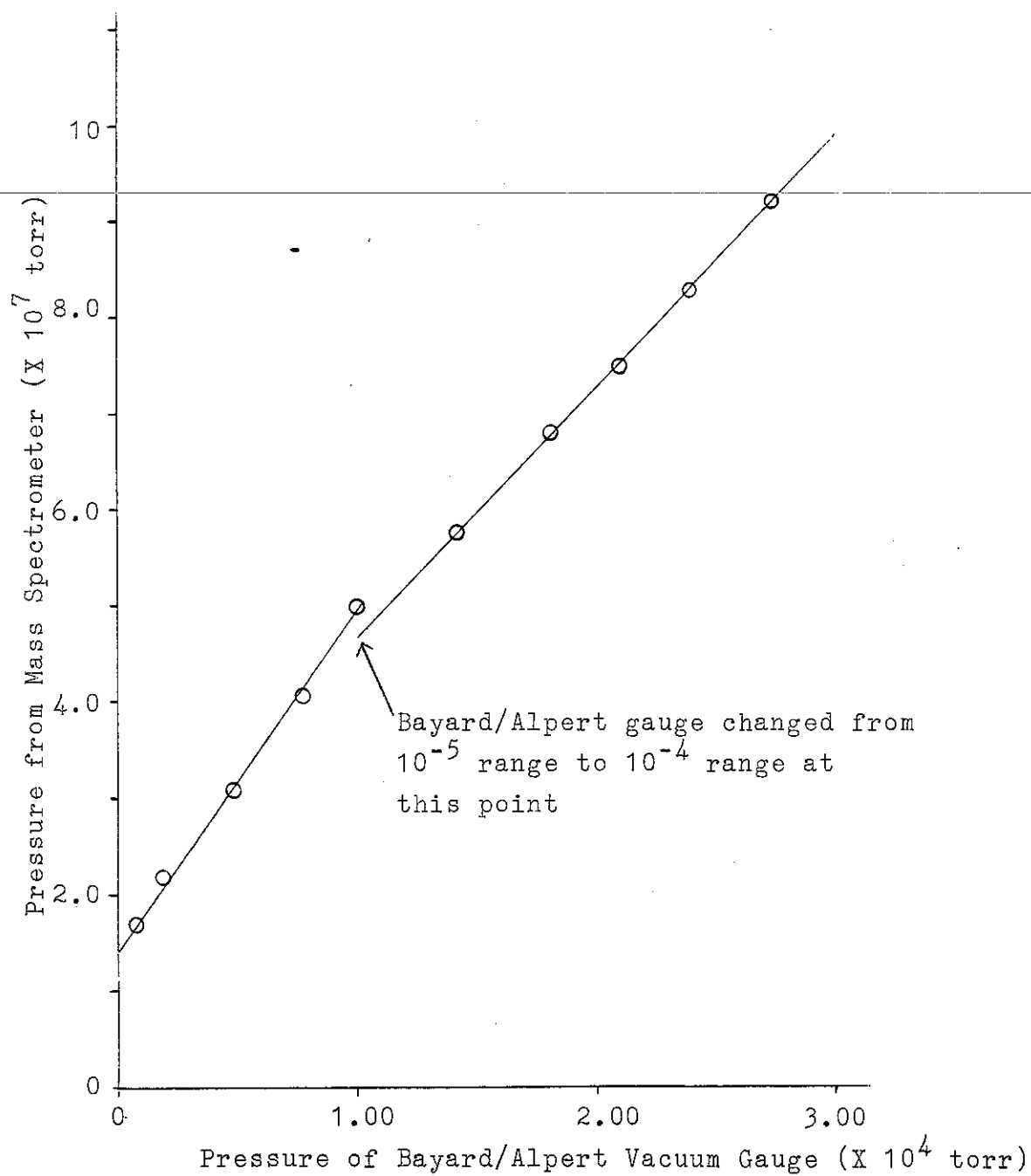
The mass spectrometer has a total pressure function which can be used to determine the pressure in the mass analyzer. When in the total pressure mode, the emission current is set at 1.0 mA. The mass filter is turned off so that all ions strike the faraday cup. The Channeltron electron multiplier is also turned off. Total pressure is then a function of the ion current and can be read directly from the instrument panel. This is factory calibrated for nitrogen.

There is a substantial pressure drop between the reaction vessel and the mass spectrometer. Therefore, the pressure reading obtainable from the mass spectrometer's total pressure function cannot be used directly to obtain the pressure in the reaction vessel. To overcome this problem, a vacuum gauge tube was mounted as shown in Figure 2.2.3. The vacuum gauge reading was then correlated with the reading of the mass spectrometer. A graph of mass spectrometer pressure versus ion gauge pressure is shown in Figure 2.3.1.1. Before doing a threshold study, the pressure of the system was recorded from the mass spectrometer and the actual reaction vessel pressure was obtained from Figure 2.3.1.1.

This could not be done for pressure studies since changing the mass spectrometer settings for each new pressure would have introduced a serious error in determining

Figure 2.3.1.1

Correlation of Mass Spectrometer  
Pressure Function with Reading from  
Bayard/Alpert Ionization Gauge



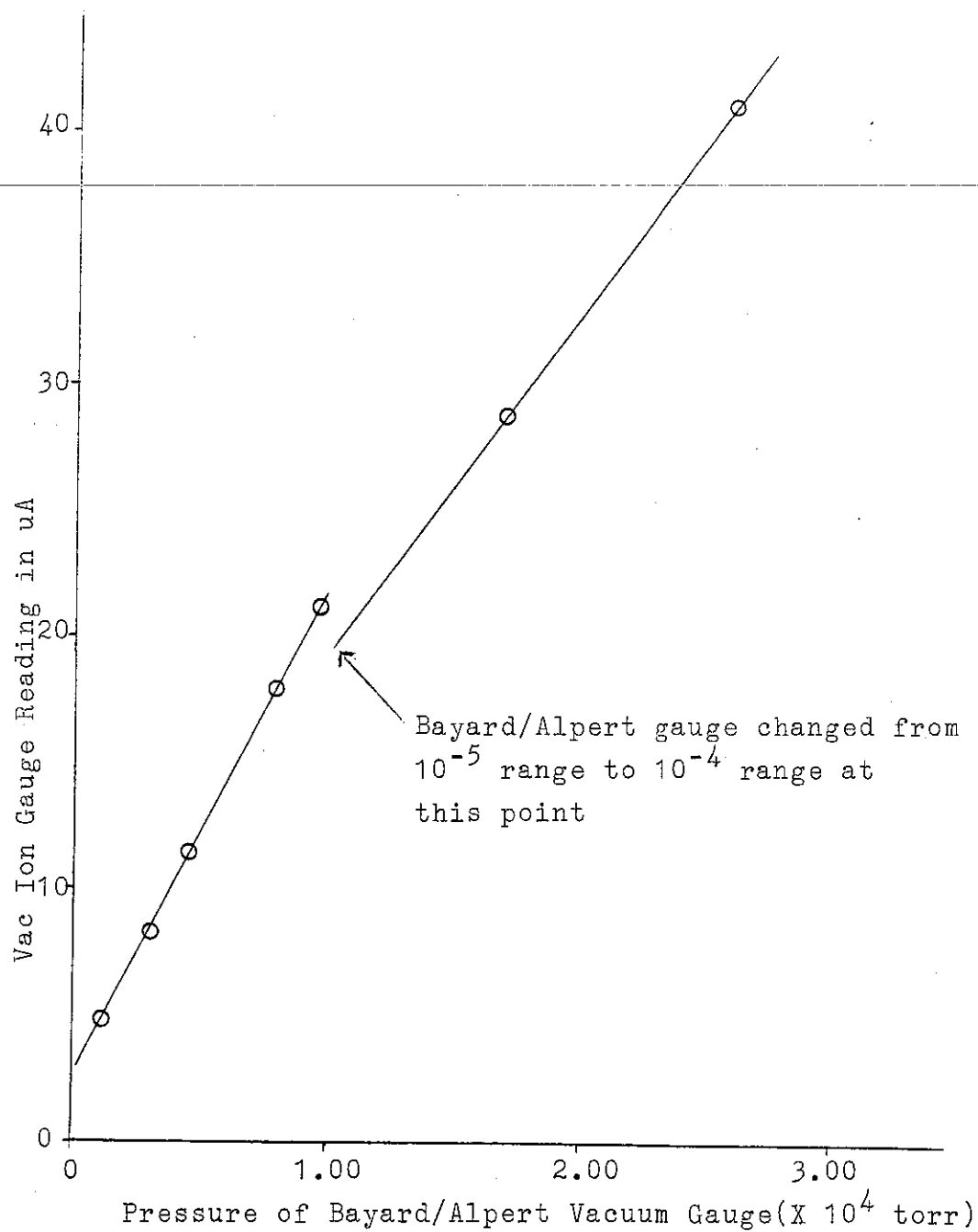
the change in ion current. Instead, the micro amp readings of the Varian Vac Ion gauge were taken to provide some indication of the pressure within the reaction vessel. A correlation was made between this reading and the Bayard/Alpert ion gauge (described earlier) and this is shown in Figure 2.3.1.2. However, the vacuum gauge reading cannot be used to obtain an accurate indication of the pressure in the reaction vessel. ~~The Varian Vac Ion gauge is linear with~~ pressure on a given day, but changes in magnitude from day to day. The accuracy is estimated to be within half an order of magnitude in units of torr.

### 2.3.2 Sample and System Preparation

Preparation for a series of experiments (either threshold or pressure studies) involves attaching a gas sample to one of the gas inlets via 10/30 glass joints (see Figure 2.2.1). The gas cylinders are equipped with their own valves (see Figure 2.2.2) which allows all four bellows valves to be open while the system is rough pumped. The leak valves are closed during this time but may be opened if it is necessary to rough pump the reaction vessel (e.g. if the system has been opened to the atmosphere). Normally, the reaction vessel is always open to the Vac Ion pump and is heated to 110 to 120 °C. After the system is rough pumped, the four bellows valves are closed. The gas cylinder valves are then opened and closed followed by opening and closing bellows valves 3 and 4. The gas is then ready to be leaked into the reaction vessel.

Figure 2.3.1.2

Correlation of Varian Vac Ion Gauge  
with Reading from Bayard/Alpert  
Ionization Gauge





When a metal surface is exposed to carbon monoxide, a layer of carbon builds up on the surface over time. To partially compensate for this, the metal surfaces were treated with oxygen to oxidize the carbon film to carbon oxides. This was followed by treatment with hydrogen to reduce any oxygen remaining on the surface to water. The procedure for this is the same as that described in section 2.3.5 for determining the effect of oxygen.

### 2.3.3 Procedure for Threshold Studies

When a sufficient current is passed through a filament, some of the electrons will gain sufficient energy to escape the filament. If a potential is placed between the filament and collector, the energies of the electrons will be the sum of this potential plus the energy with which they escape the filament (see section 3.1). In a threshold study, the effect of the electron energy on the intensity of a given mass level at a given temperature and pressure is determined while carbon monoxide gas is passed through the reaction vessel.

Unfortunately, it was not possible simply to monitor the intensity of a peak while the potential was increased or decreased. The pressure in the system could not be kept absolutely constant during a run and the instrument drifted slightly. The procedure given in the following paragraphs compensates for these problems.

First, the reaction vessel filament was turned on

and allowed to warm up for at least fifteen minutes. The filament current was set so the emission current was 0.110 to 0.125 mA at 8.00 V potential difference. At this setting the retarding potential necessary for complete suppression of residual current varied from 0.0 to 0.4 V depending on the filament, its age and the filament current.

Before a gas flow was established, the pressure of the background gases was determined. The pressure was found to vary from  $1.5 \times 10^{-7}$  to  $2.5 \times 10^{-7}$  torr from day to day as determined from the mass spectrometer's total pressure function. The gas flow was then established at some constant pressure. Generally, it took from five to ten minutes before the pressure was found to stay approximately constant. The emission current did not appear to be affected by the flow of carbon monoxide gas.

The mass spectrometer was then set for the mass level of interest and the electron multiplier gain (amplitude), emission current, damper and resolution were adjusted. All these adjustments were kept identical for a given mass level with different metal surfaces to allow for more effective comparison.

As shown in Figure 2.2.5, the potential across the filament and collector could be removed by throwing a double-pole switch. When the switch is reversed, the potential is removed and the circuit is shorted. This gives effectively zero volts acceleration to the electron beam.

A run was then done in which the change in intensity

of the ion current was determined as a function of potential.

For each potential this was done as follows:

1. The switch was set in the open position and the ion current was monitored until the signal was stable (five to twenty seconds).
2. The computer was commanded to collect 200 samples of the ion current at 35 samples per second.
3. The switch was set in the applied potential position and the ion current was monitored until the signal was stable (five to twenty seconds).
4. The computer was commanded to collect 200 samples of the ion current at 35 samples per second.
5. Steps 1 through 4 were repeated.
6. A final collection of the ion current was taken in the open position.

At the end of this procedure the computer will have stored, on disk, five sets of data with two hundred values in each set. Three sets would correspond to no potential applied and two sets would correspond to potential applied. The two hundred values per set were collected to allow the computer to determine average values. This filtered out high frequency noise.

The change in intensity was determined by having the computer output the average values of the five sets. The change in intensity was then taken as the difference between successive average values of the ion current with and without potential applied. This yielded four values for the change in intensity at a given potential. The average of these four values was then taken. Four samples were determined to compensate for pressure changes and electronic drift which both occur when taking samples.

The set of data provided in Table 2.3.3.1 will help illustrate the above. The error limit was determined by

Table 2.3.3.1

The Change in Ion Current at 68 amu  
 Measured as a Function of Electron Energy  
 -Typical Set of Data for Carbon Monoxide  
 Adsorbed on a Metal Surface-

Potential	Average of 200 Samples of Ion Current	Difference Between Successive Values	Average of Differences	Average Deviation of Differences
0.00	1137			
1.00	1121	-10		
0.00	1120	1	1	6
1.00	1122	2		
0.00	1110	12		
0.00	1107			
2.00	1107	0		
0.00	1107	0	3	4
2.00	1107	0		
0.00	1097	10		
0.00	1093			
3.00	1088	-5		
0.00	1082	6	3	5
3.00	1091	9		
0.00	1090	1		
0.00	1083			
4.00	1084	1		
0.00	1079	5	4	1
4.00	1083	4		
0.00	1078	5		
0.00	1078			
5.00	1082	4		
0.00	1073	9	6	2
5.00	1078	5		
0.00	1073	3		
0.00	1066			
6.00	1083	17		
0.00	1062	21	14	5
6.00	1074	12		
0.00	1069	5		
0.00	1061			
7.00	1079	18		
0.00	1060	19	20	2
7.00	1082	22		
0.00	1061	21		

Table 2.3.3.1 (continued)

Potential (in Volts)	Average of 200 Samples of Ion Current	Difference Between Successive Values	Average of Differences	Average Deviation of Differences
0.00	1057	29		
8.00	1086	30		
0.00	1056	28	29	1
8.00	1084	30		
0.00	1054			
0.00	1051	48		
9.00	1099	47		
0.00	1052	49	48	1
9.00	1101	46		
0.00	1055			

Error limit = Average of Average Deviations = 3

determining the average deviation of each set of four values. The average of these average deviations was taken as the error limit.

#### 2.3.4 Procedure for Pressure Studies

These studies were conducted in a manner similar to that described for the potential studies. Instead of varying the potential, the pressure was varied. Five sets of data containing two hundred samples of the ion current in each set were collected for each pressure. Three sets corresponded to zero potential and two sets corresponded to 8.00 V potential. The sets were collected, at different pressures, in a manner identical to that described for the threshold studies.

The potential necessary for complete suppression of emission current varied from 0.0 to 0.4 V. This variation is not considered important for pressure studies. The value of 8.00 V was selected because it is as high as it was safe to go without ionization events becoming a real concern.

The pressure was monitored with the Vac Ion gauge on the Varian Vac Ion pump since it was not practical to use the mass spectrometer's total pressure function for the reasons given previously.

#### 2.3.5 Procedure for Determining the Effect of Oxygen

Oxygen gas was placed in the reaction vessel at approximately 0.25 to 0.50 atm and baked at 200 to 230 °C for approximately 3½ hours. The system was then rough

pumped until the reaction vessel could be opened to the mass spectrometer. The reaction vessel was then pumped down with the Vac Ion for 48 hours. During this time the filament was occasionally turned on at approximately 0.2 mA emission current and 40 V applied potential. This was done to help the system degas. At the end of 48 hours, the background at 44 amu was low enough to allow a potential study. This was done according to the procedure given in section 2.3.3.

The reaction vessel was then treated with hydrogen gas in a manner similar to that described for oxygen gas. However, only 24 hours were required to bring the background at 44 amu down to acceptable levels. The background at 18 amu was observed to decrease significantly during this time.

## Chapter 3

### Data and Results

#### 3.1 Filament Characterization

When sufficient current is passed through a filament, thermionic emission of electrons results. The energy of these electrons is described by a Boltzmann distribution and the potential necessary to suppress the emission current to zero (less than  $0.1 \mu\text{A}$  in this case) is a measure of the width of this distribution. This will be referred to as the suppression potential.

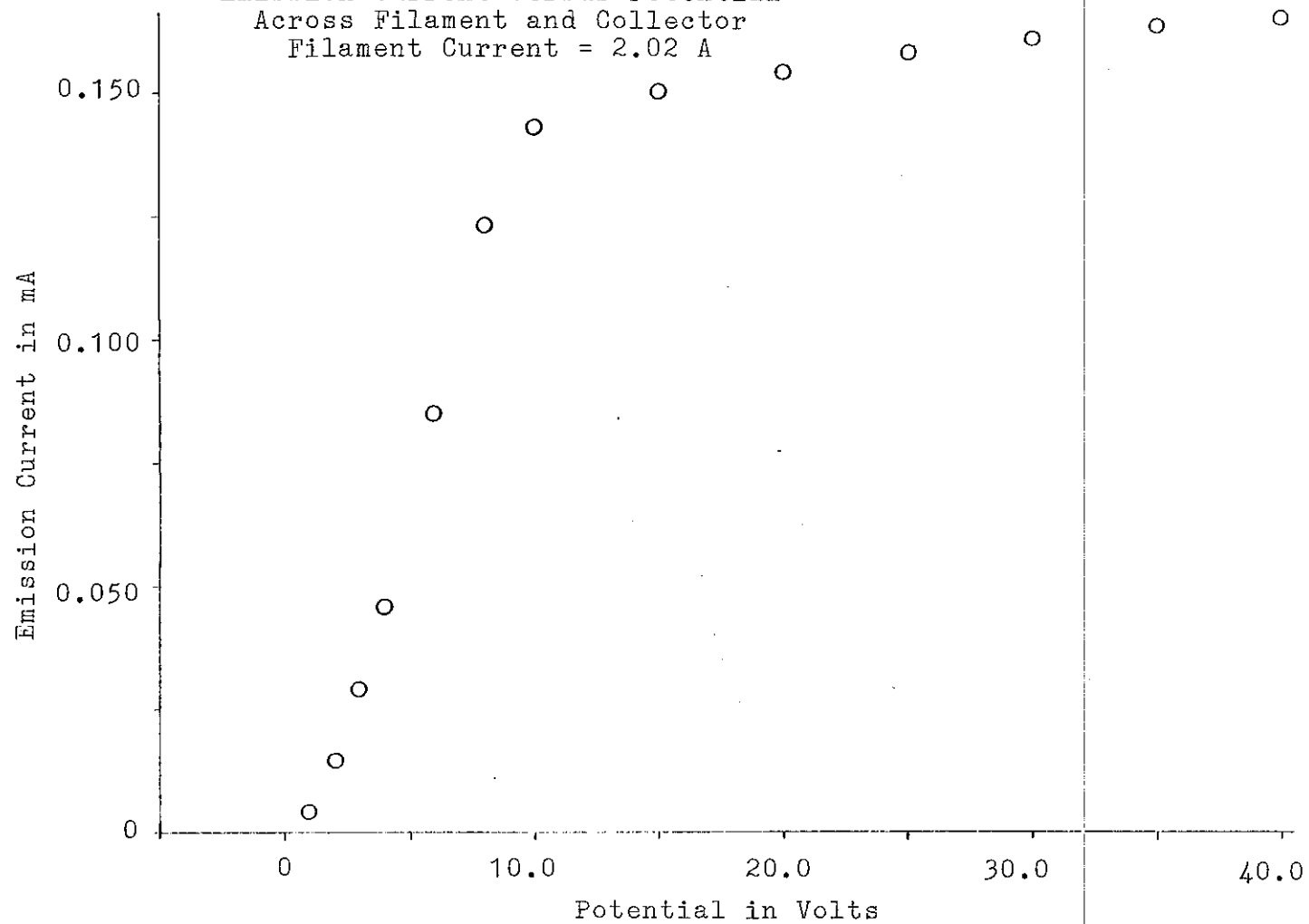
As explained in the experimental section, the filament current was set so that the emission current was  $0.110$  to  $0.125 \text{ mA}$  at  $8.00 \text{ V}$  potential difference. A typical plot of emission current versus potential difference is shown in Figure 3.1.1 for these parameters. When a given thoriated iridium filament is first operated, the suppression potential under these conditions is zero. As the filament ages, the suppression potential gradually increases. This necessitates a correction factor when the change in ion current for a given mass level is measured as a function of potential difference. All potentials in the pages that follow have been corrected.

Note that the region between  $3.0$  and  $8.0 \text{ V}$  of Figure 3.1.1 is approximately linear. This is important since onset potentials are being determined graphically in the pages that



Figure 3.1.1

Emission Current Versus Potential  
Across Filament and Collector  
Filament Current = 2.02 A



follow. If a threshold event is occurring, it should have a sudden onset and should increase approximately linear with potential. The linearity of this region is clearly shown in Figure 3.1.2.

### 3.2 Threshold Studies

The effect of potential on the ion current was determined at 44, 56 and 68 amu for gold, nickel, palladium and molybdenum metal films. Mass spectrometer settings were kept constant for studies at a given mass level and the resolution was always unit mass or better. The threshold behavior at 40 amu could not be determined because of the high background.

In the following pages, the change in ion current intensity as a result of applied potential will be indicated as  $\Delta I_x$  where x is the mass level being observed. Thresholds are determined by drawing the best straight lines through the points before and after the threshold and taking the intersection of the two lines as the threshold. Most studies were done at 110 to 120 °C but occasionally the temperature was increased to determine its effect. The pressure of carbon monoxide in the reaction vessel is indicated as  $P_{CO}$  in the following pages.

Figures 3.2.1 through 3.2.6 show the effect of potential on ion current at 44 amu over the potential range of 0.0 to 40.0 V. Each graph shows one maximum and one minimum. The maximum occurs between 1.0 and 3.0 V while the minimum occurs between 5.0 and 8.0 V, depending on the metal. This

Figure 3.1.2

Emission Current Versus Potential  
Across Filament and Collector  
from -1.00 to 8.00 V  
Filament Current = 2.03 A

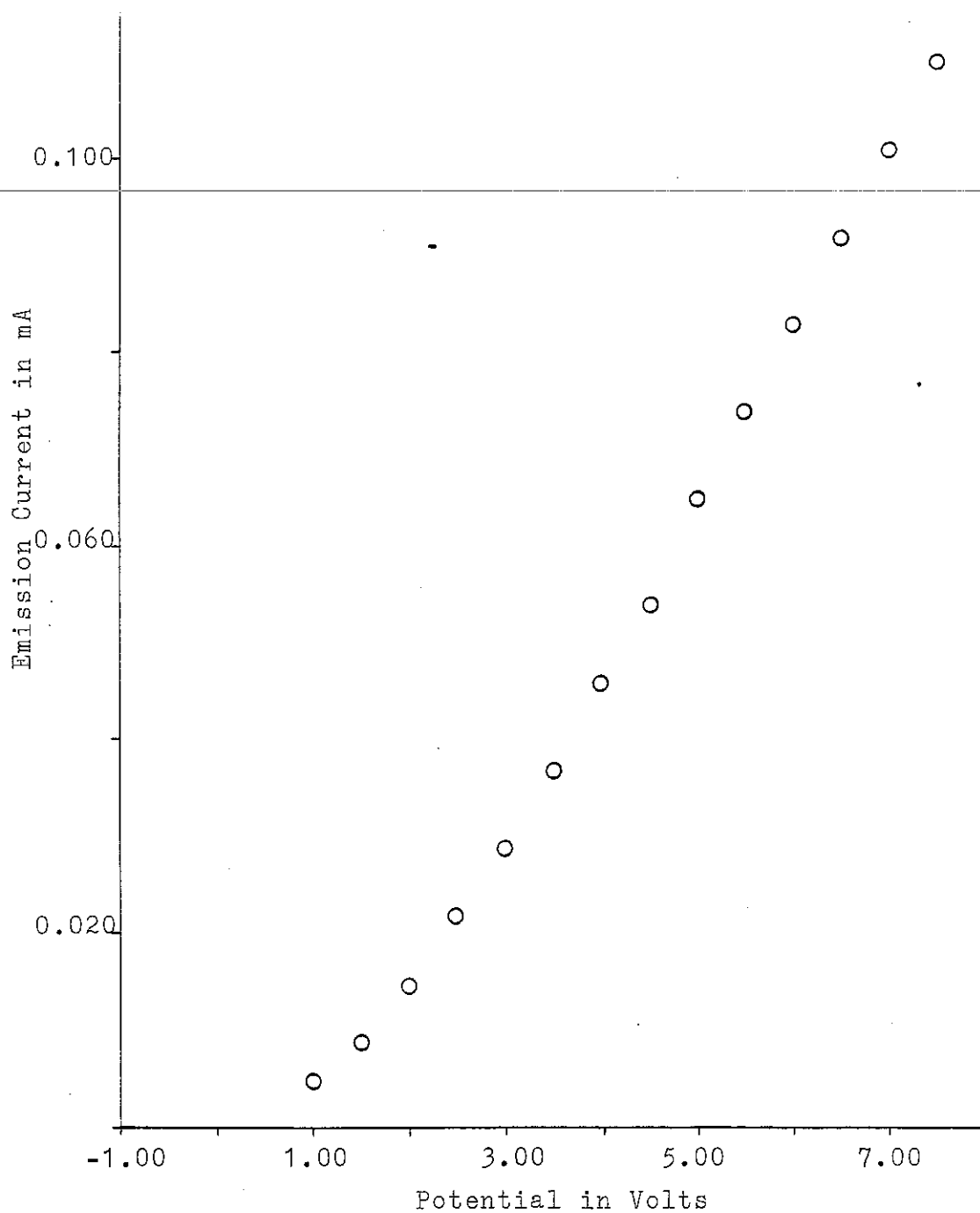


Figure 3.2.1

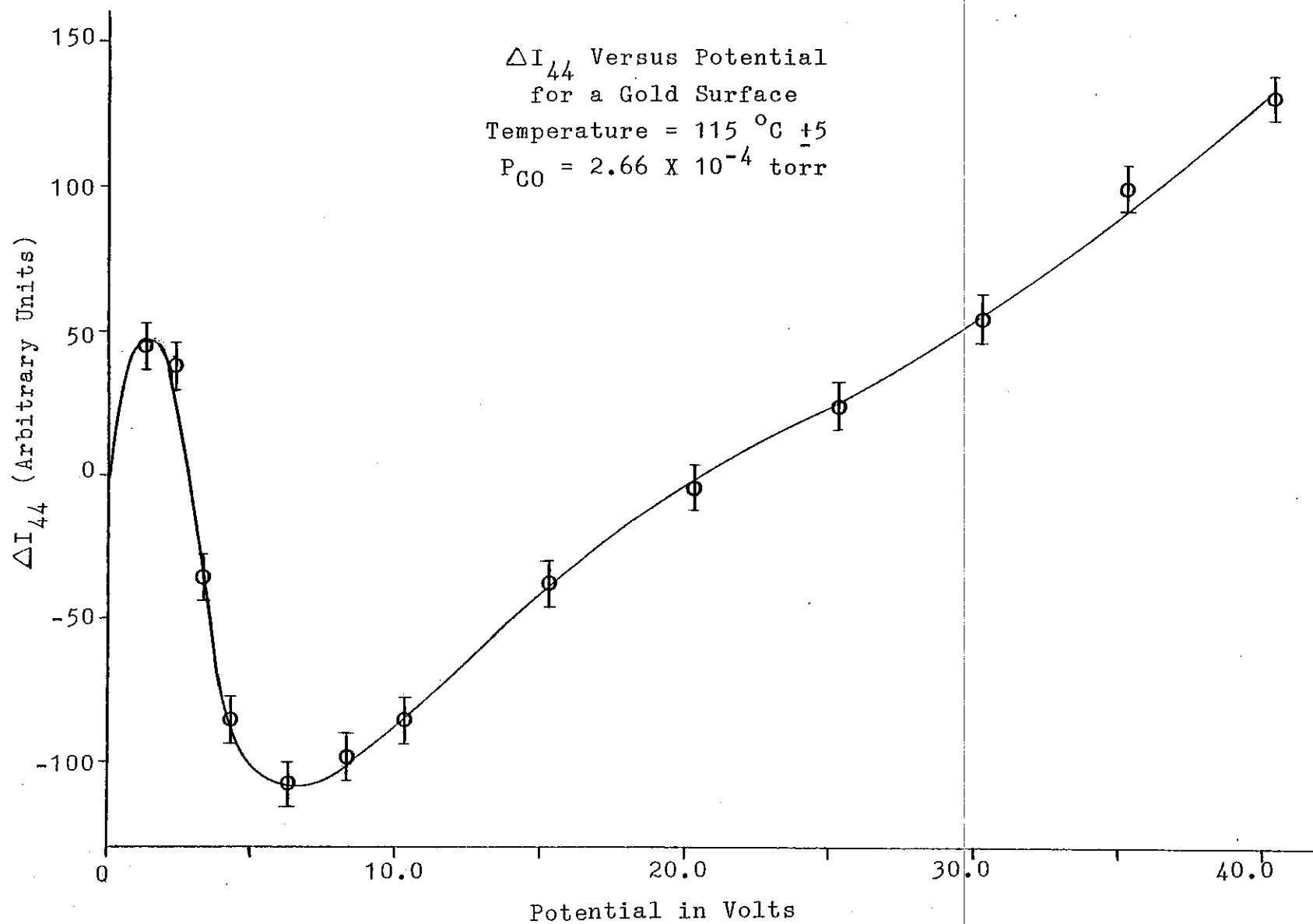


Figure 3.2.2

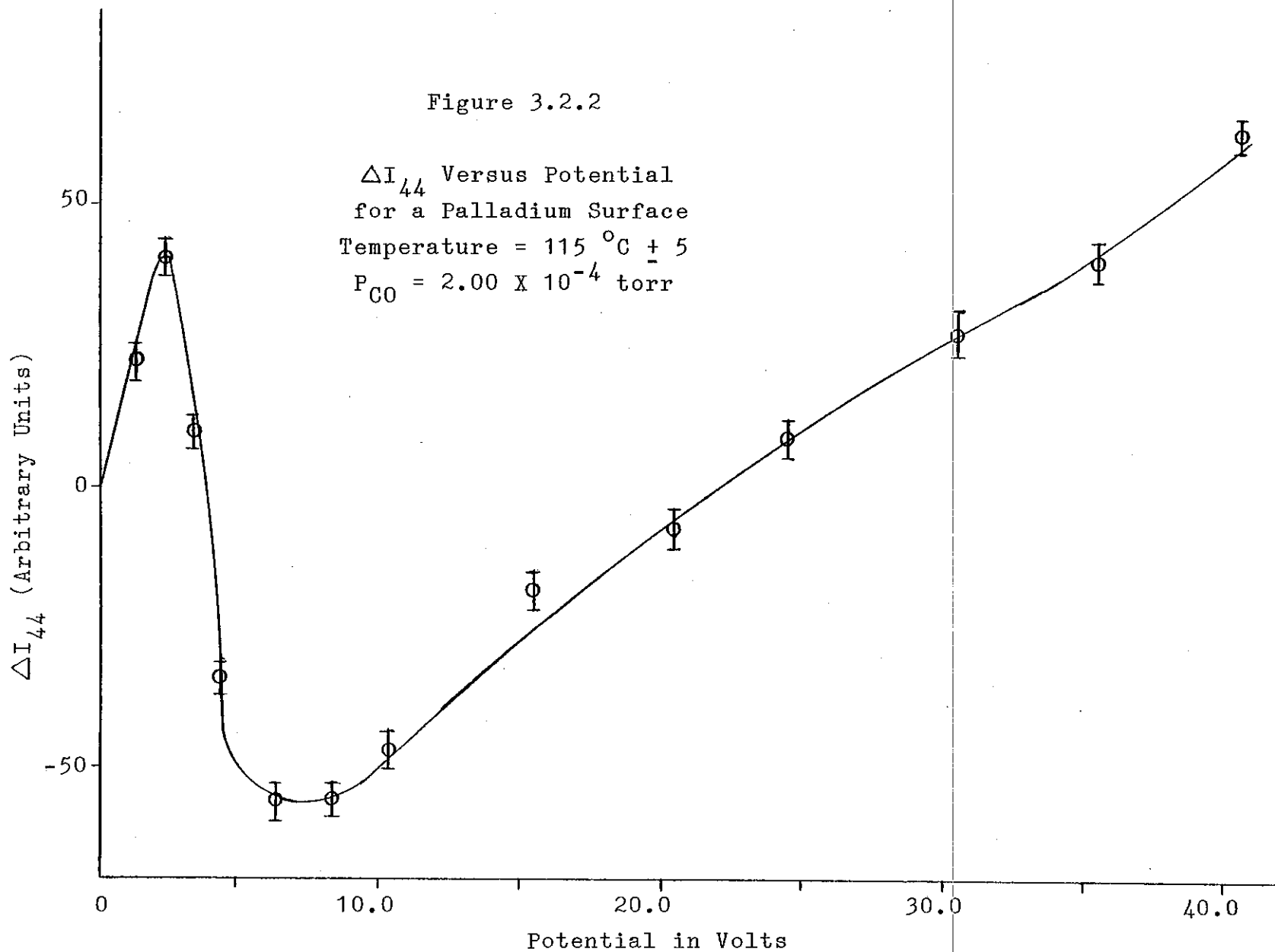


Figure 3.2.3

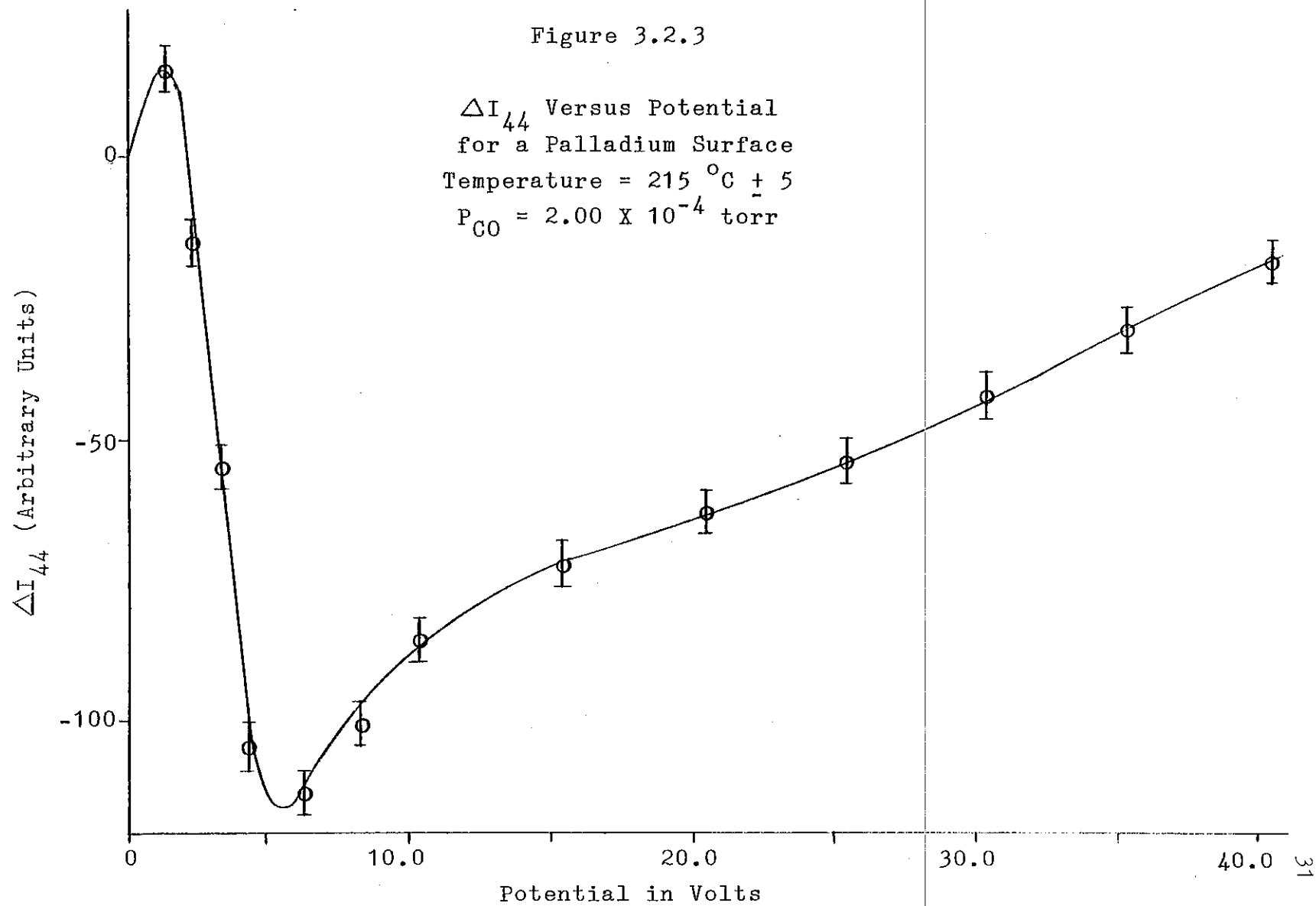
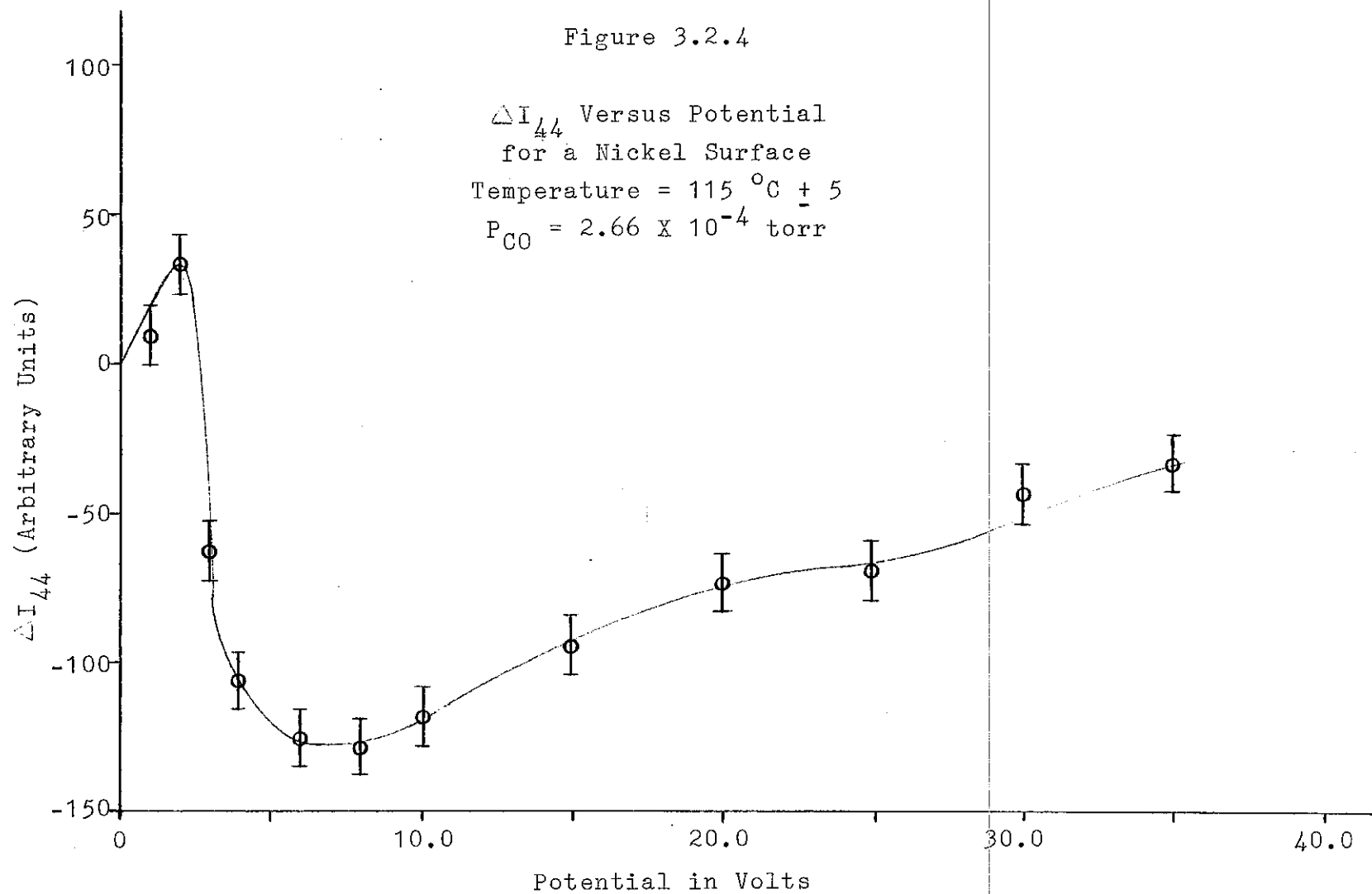


Figure 3.2.4



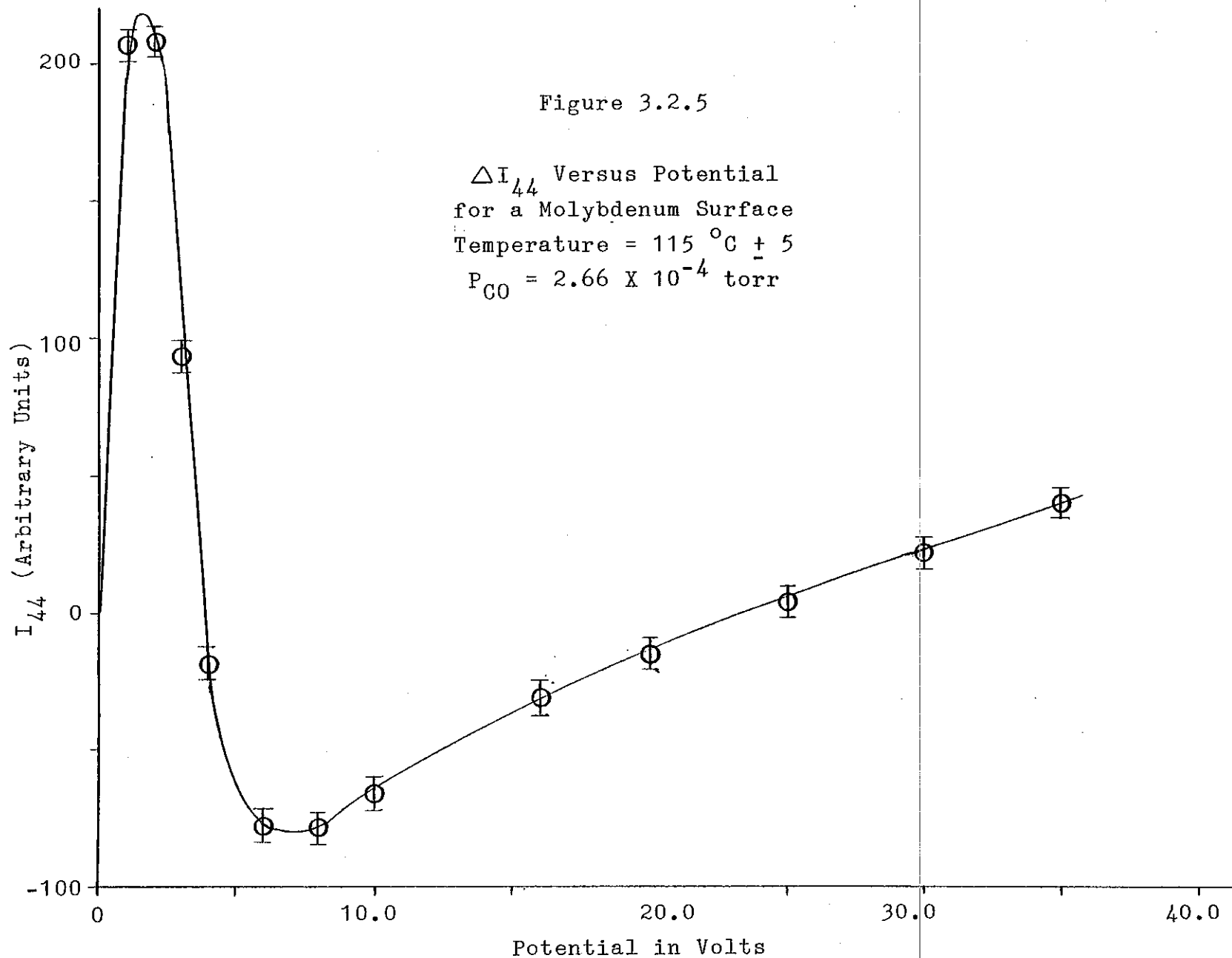
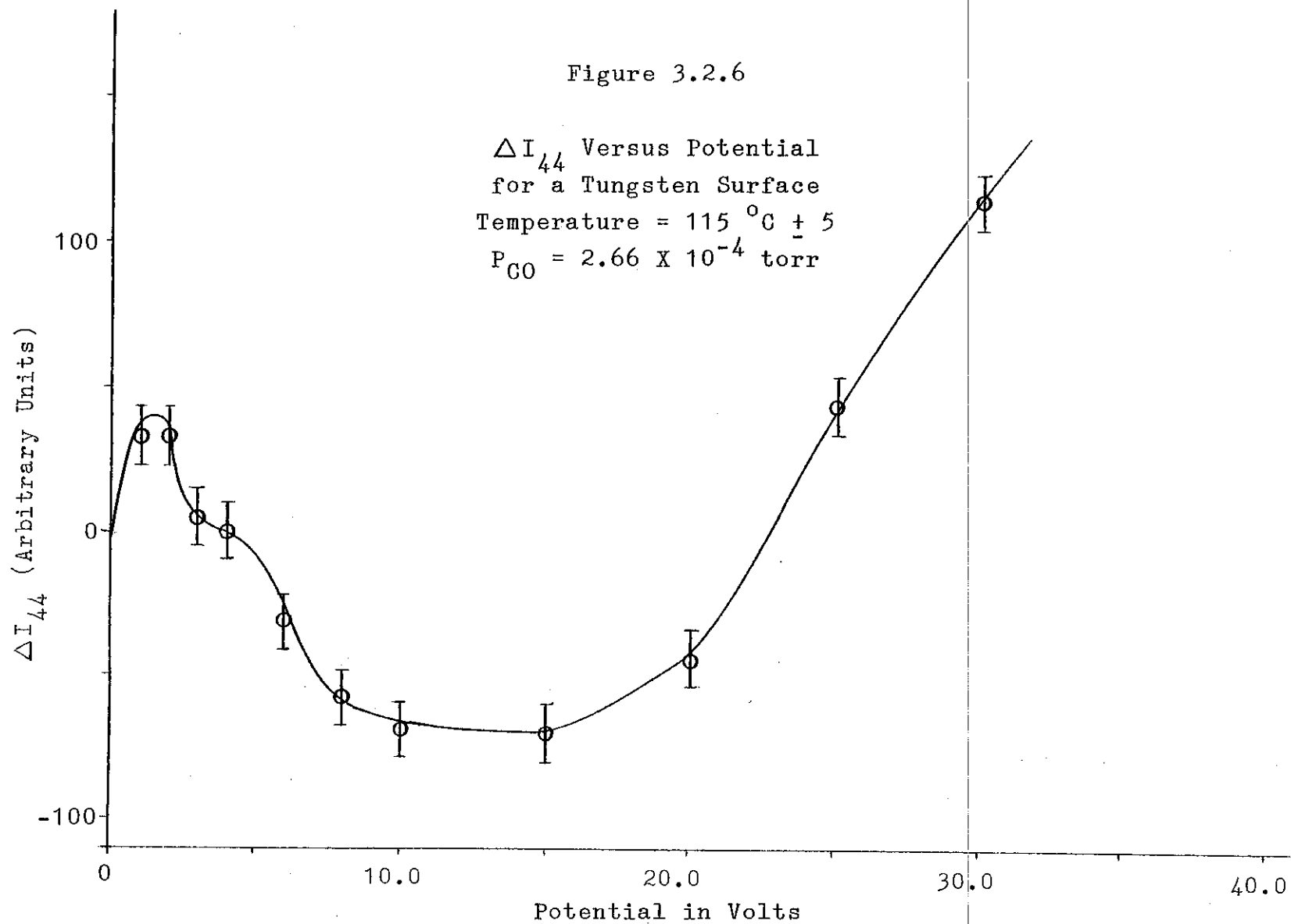




Figure 3.2.6



is presented in Table 3.2.1. No real trend was established from these results. Generally, they all have the same shape with the exception of Tungsten which has an inflection point. The effect of increasing the temperature of the palladium surface is to shift the maximum to a lower potential and decrease its intensity. In all cases,  $\Delta I_{44}$  is positive at low potentials and becomes negative with increasing potential. At some point, the negative change at  $\Delta I_{44}$  becomes less pronounced and eventually becomes positive once again.

It is not possible to determine accurate threshold values from these experiments because of the large potential increments. For this reason, more careful studies were done between 2.5 and 9.0 V and these are presented in Figures 3.2.7 through 3.2.11 for 44 amu. The behavior of  $\Delta I_{44}$  is complicated compared to  $\Delta I_{56}$  and  $\Delta I_{68}$ . For this reason, less weight was given to the results obtained at 44 amu when the mechanism of electron impact excitation was considered.

Threshold values at 56 and 68 amu are presented in Figures 3.2.12 through 3.2.20 and the thresholds are indicated on the graphs. All the threshold results have been tabulated in Table 3.2.2.

### 3.3 Pressure Studies

The dependence of  $\Delta I_x$  on pressure was only studied for carbon monoxide adsorbed on palladium. Complete potential (threshold) studies were done at three pressures for mass level 44. These are shown in Figures 3.3.1 through

Table 3.2.1

Maximums and Minimums of  
Figures 3.2.1 through 3.2.6

Surface	Temperature ( $\pm 5^\circ\text{C}$ )	Location of Maximum (Volts)	$\Delta I_{44}$ at Maximum	Location of Minimum (Volts)	$\Delta I_{44}$ at Minimum
Gold	115	1.79	50	6.29	-107
Palladium	115	2.17	41	7.77	-56
"	215	1.42	15	6.37	-113
Nickel	115	2.35	34	7.35	-128
Molybdenum	115	1.50	215	7.10	-78
Tungsten	115	1.40	37	11.80	-70

Figure 3.2.7

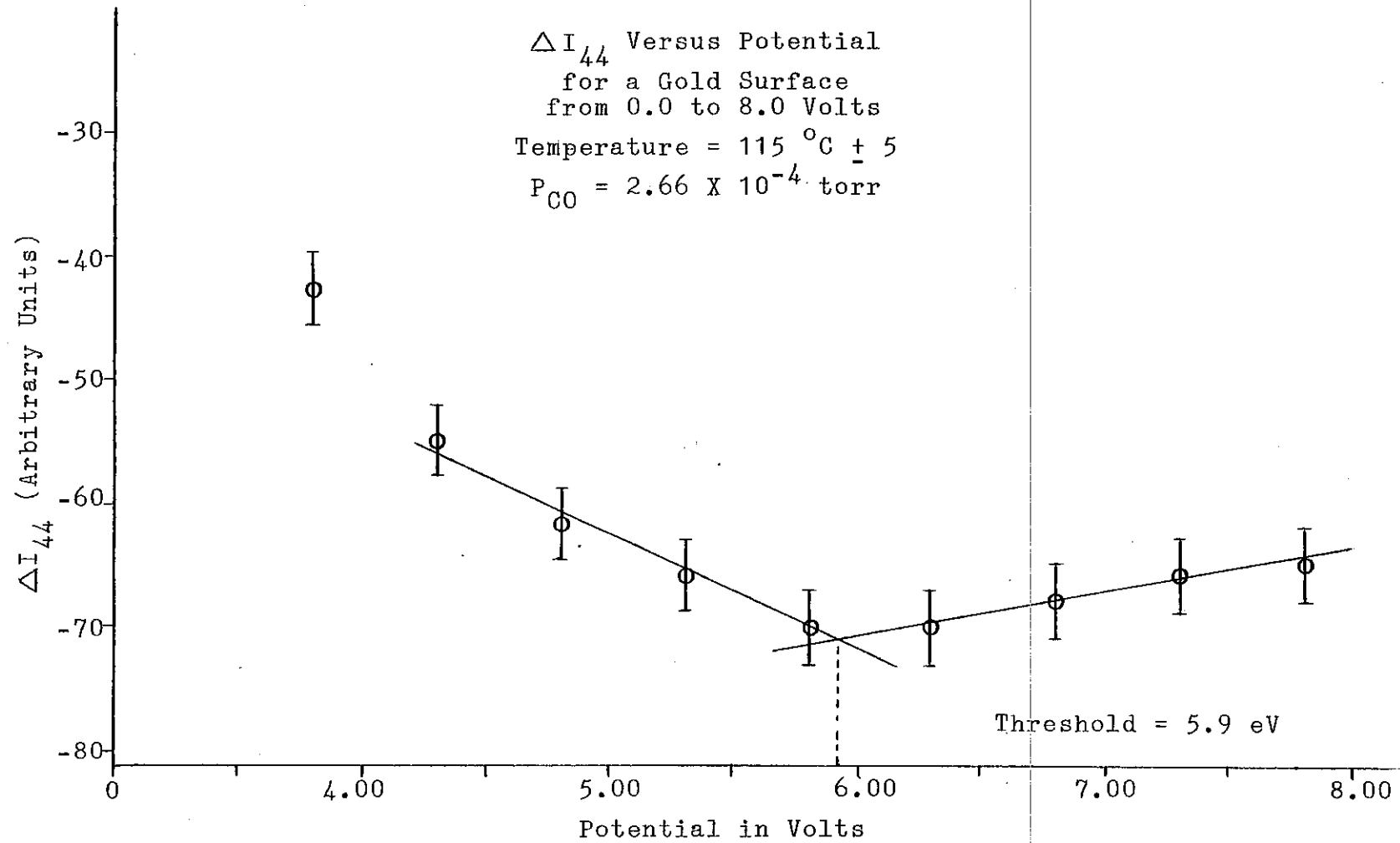


Figure 3.2.8

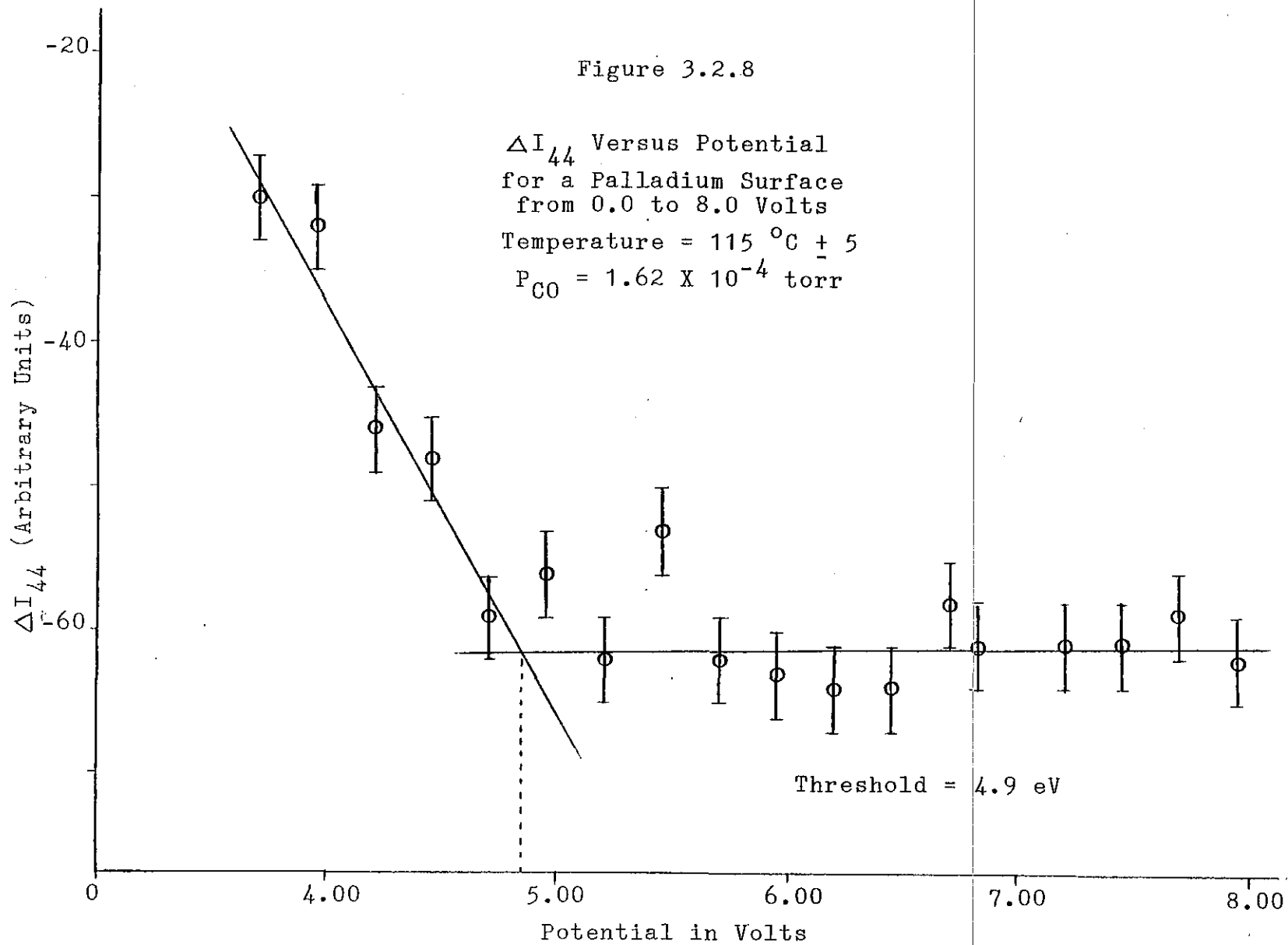


Figure 3.2.9

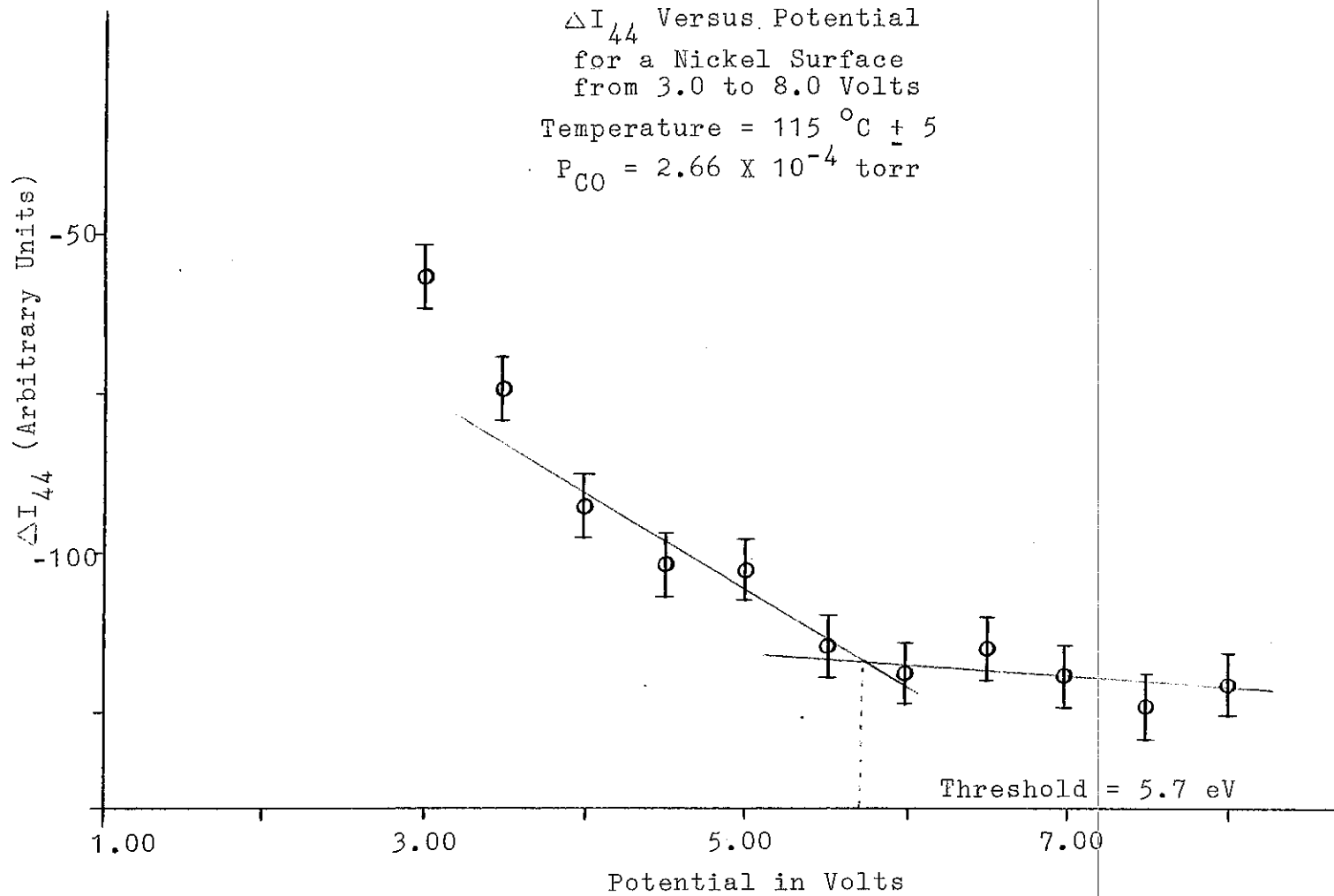


Figure 3.2.10

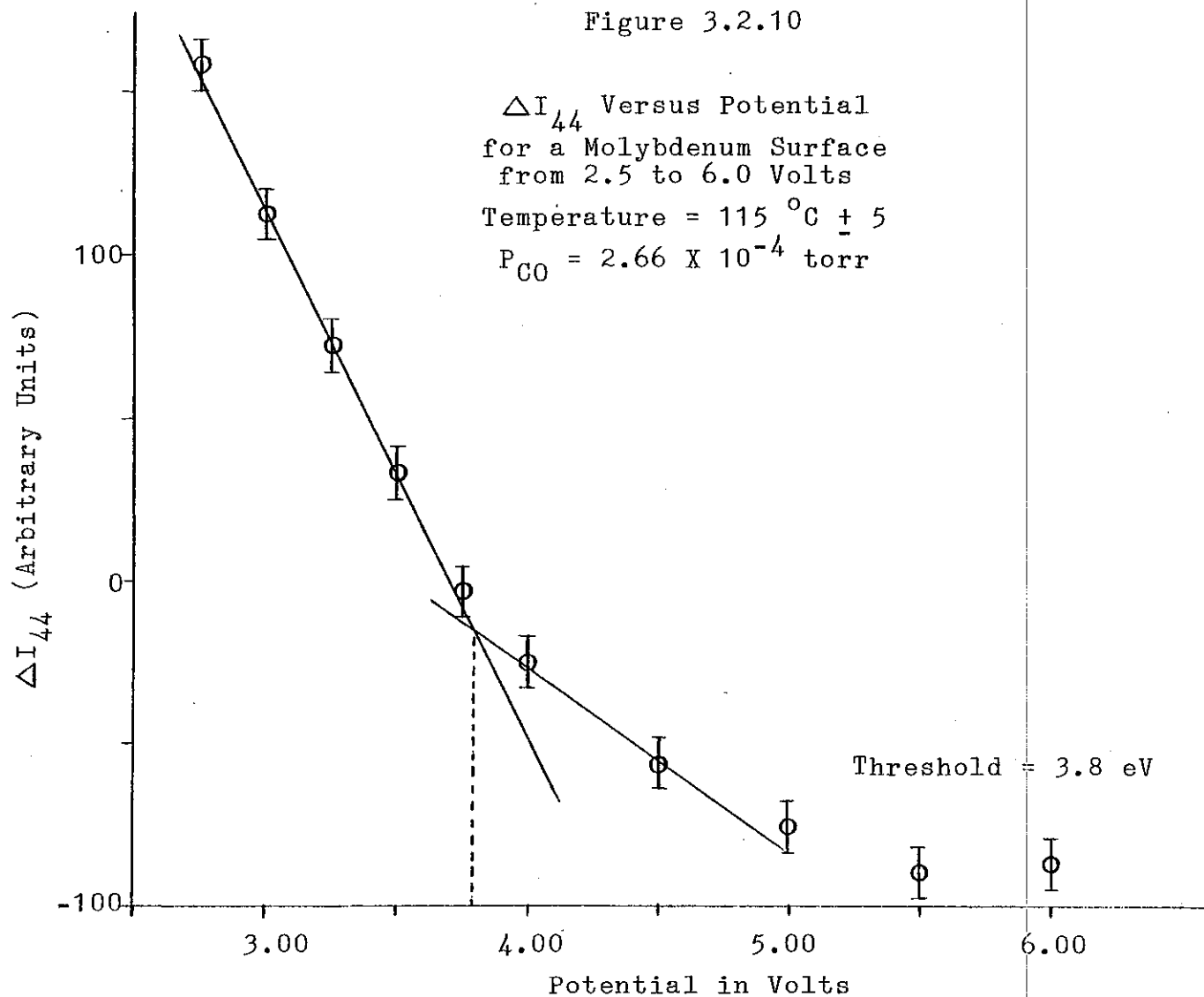
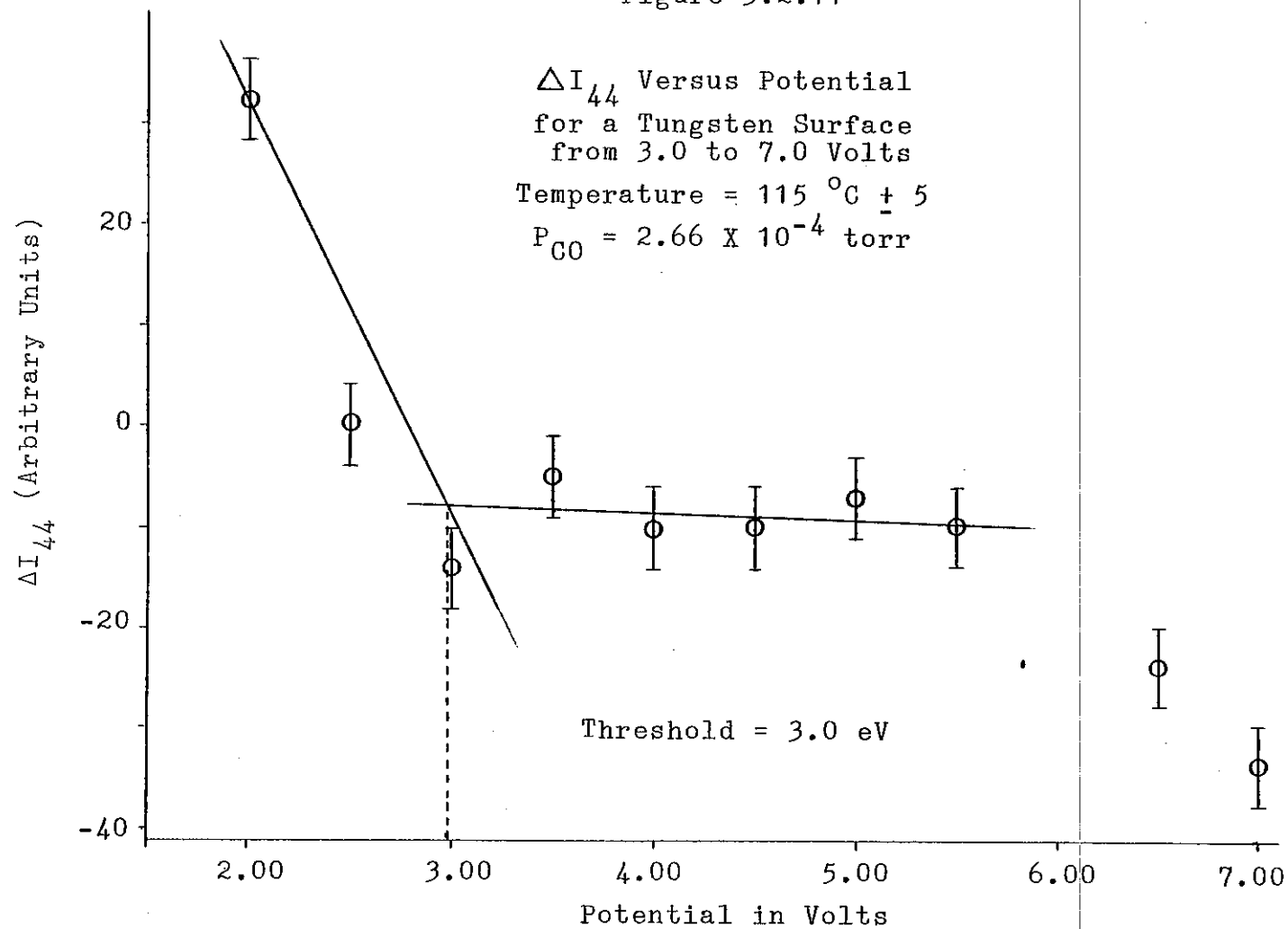


Figure 3.2.11





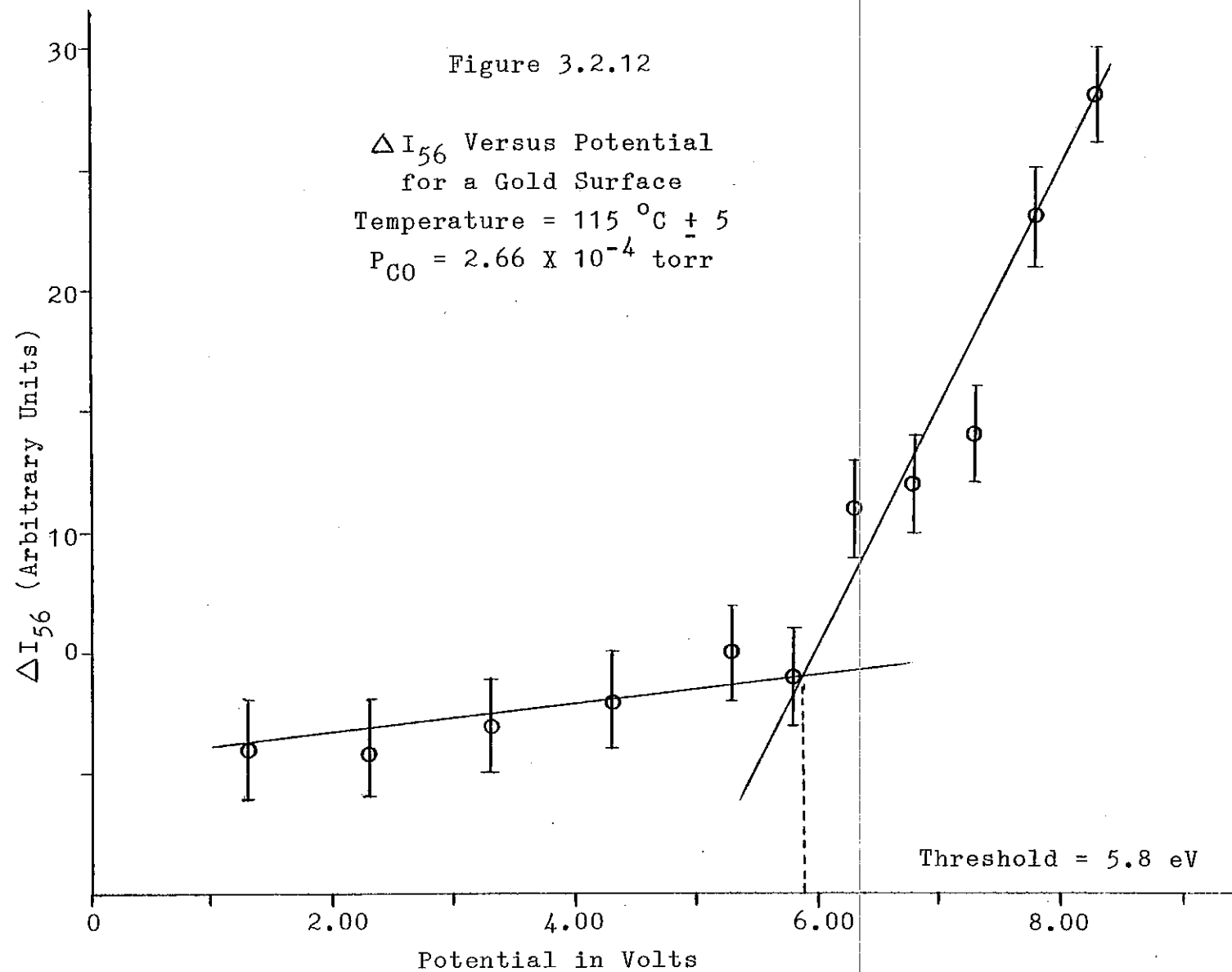


Figure 3.2.13

$\Delta I_{56}$  Versus Potential  
for a Palladium Surface  
at Two Temperatures

$P_{CO} = 2.00 \times 10^{-4}$  torr

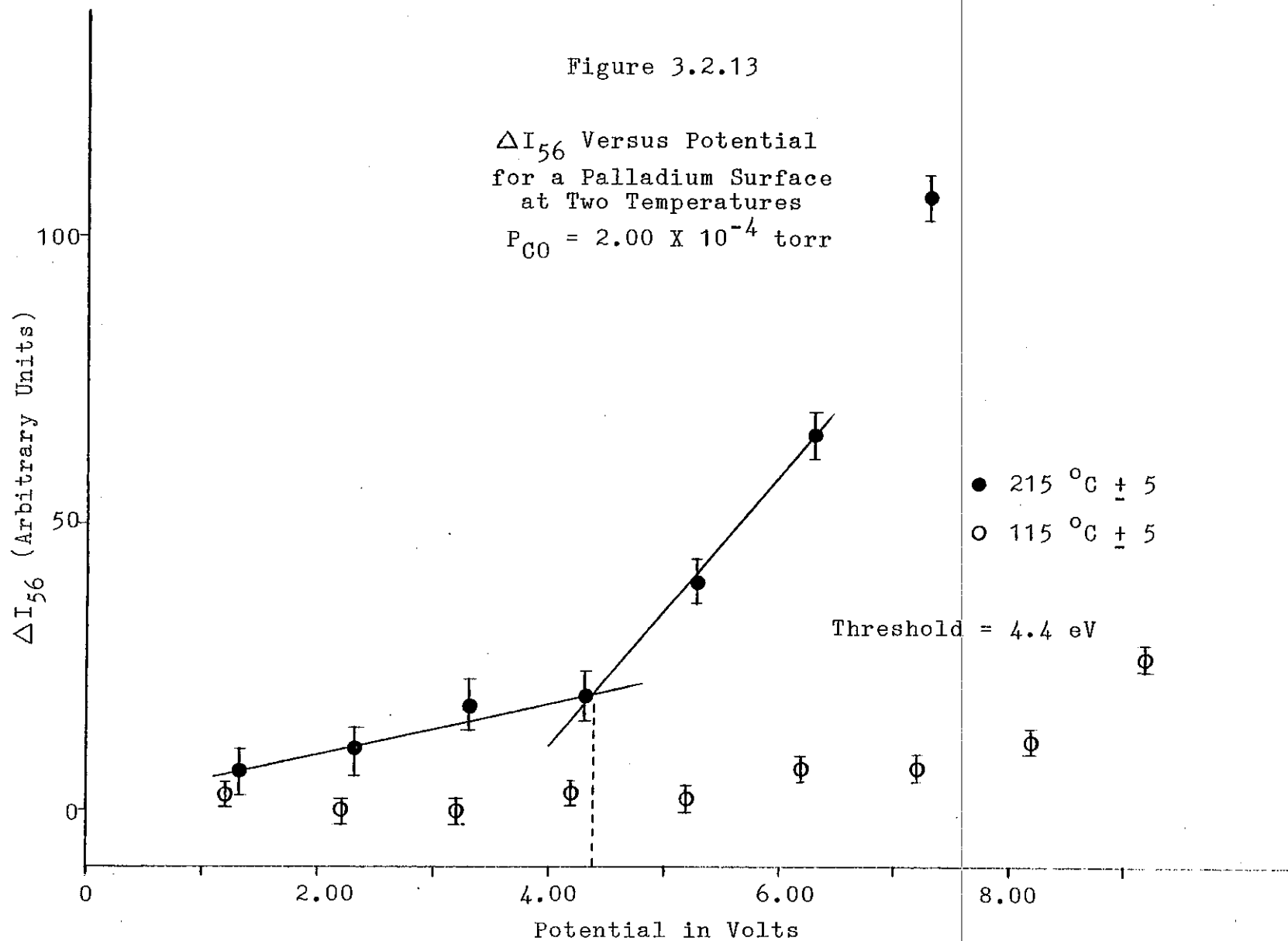


Figure 3.2.14

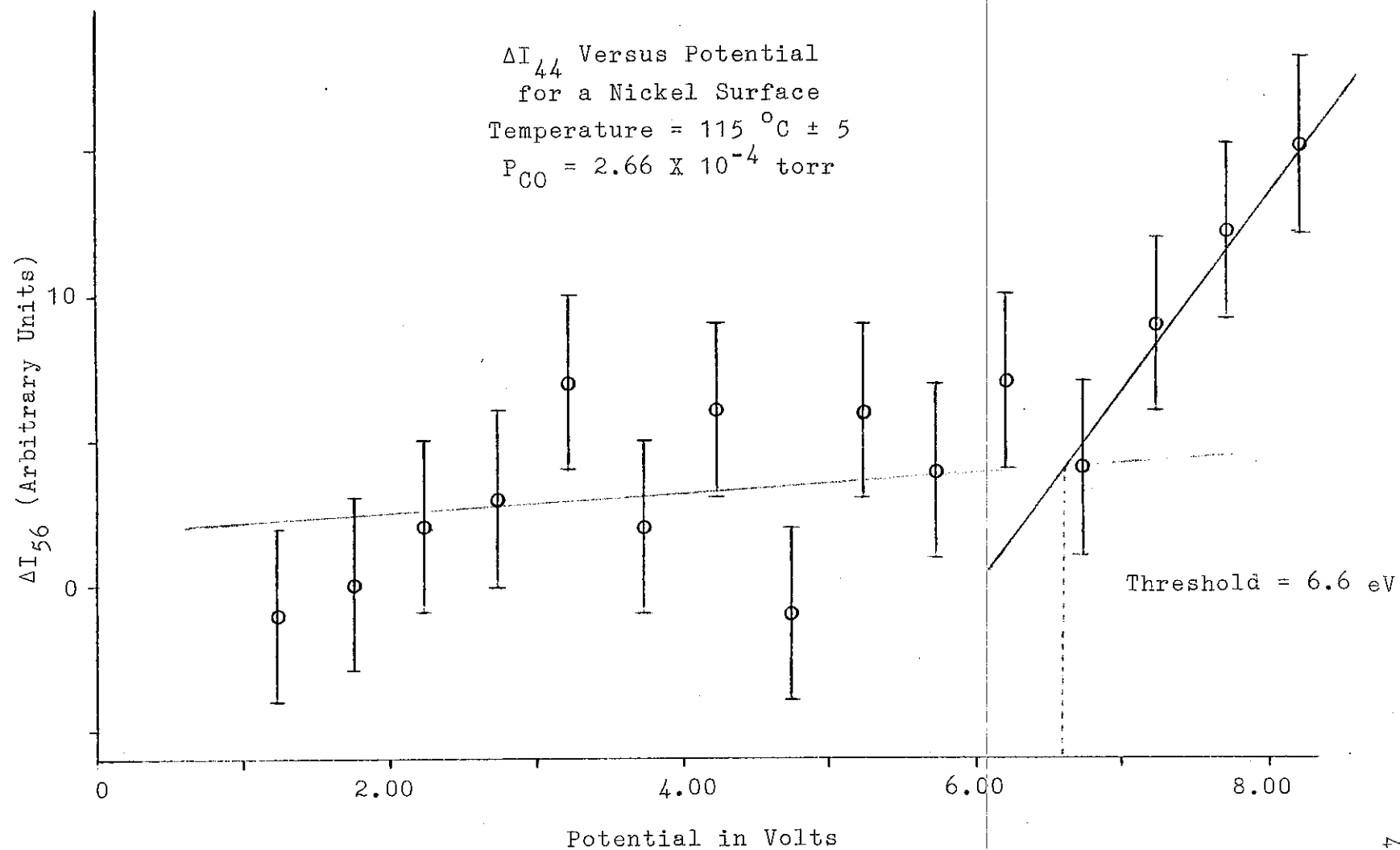


Figure 3.2.15

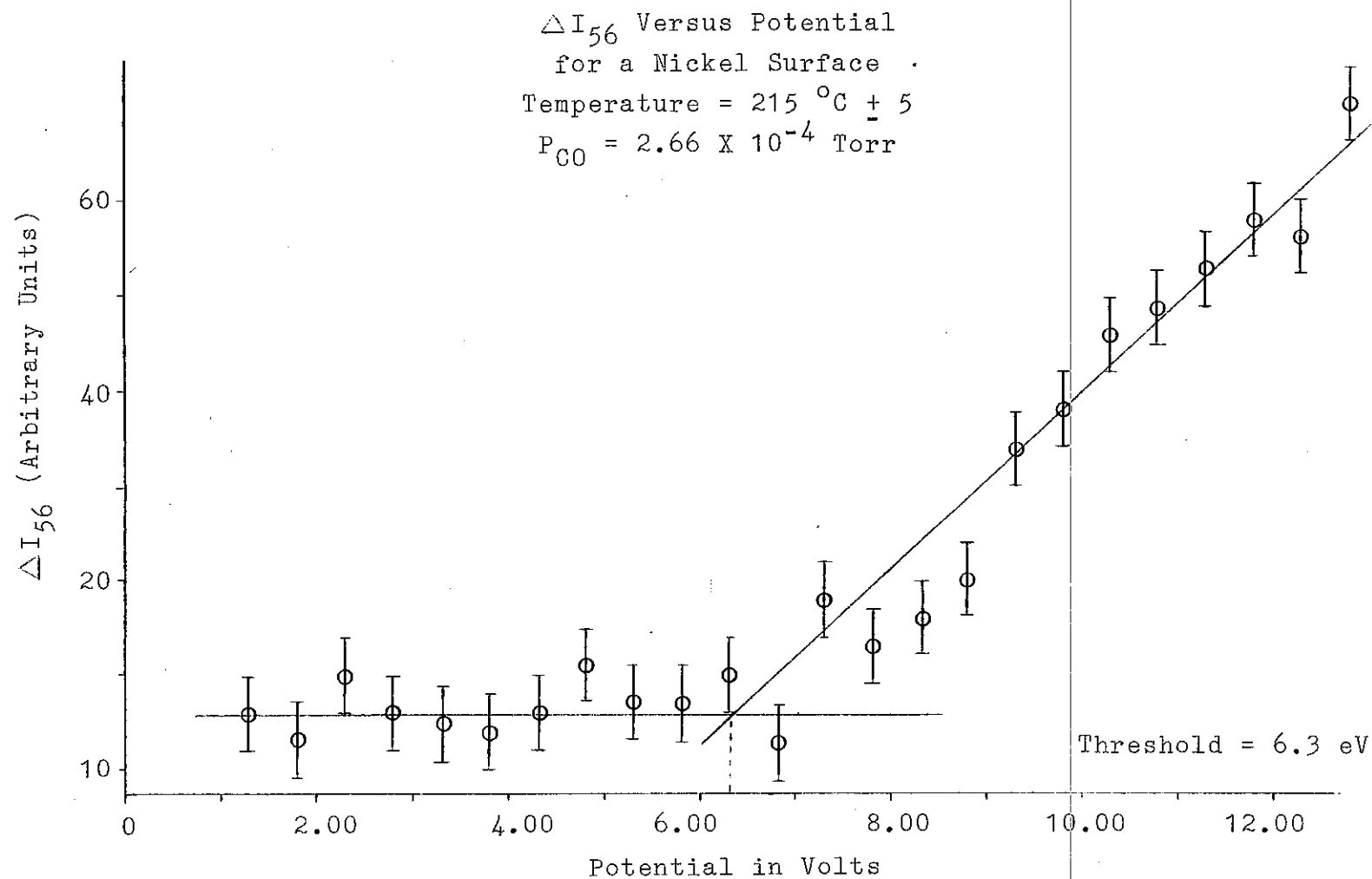


Figure 3.2.16

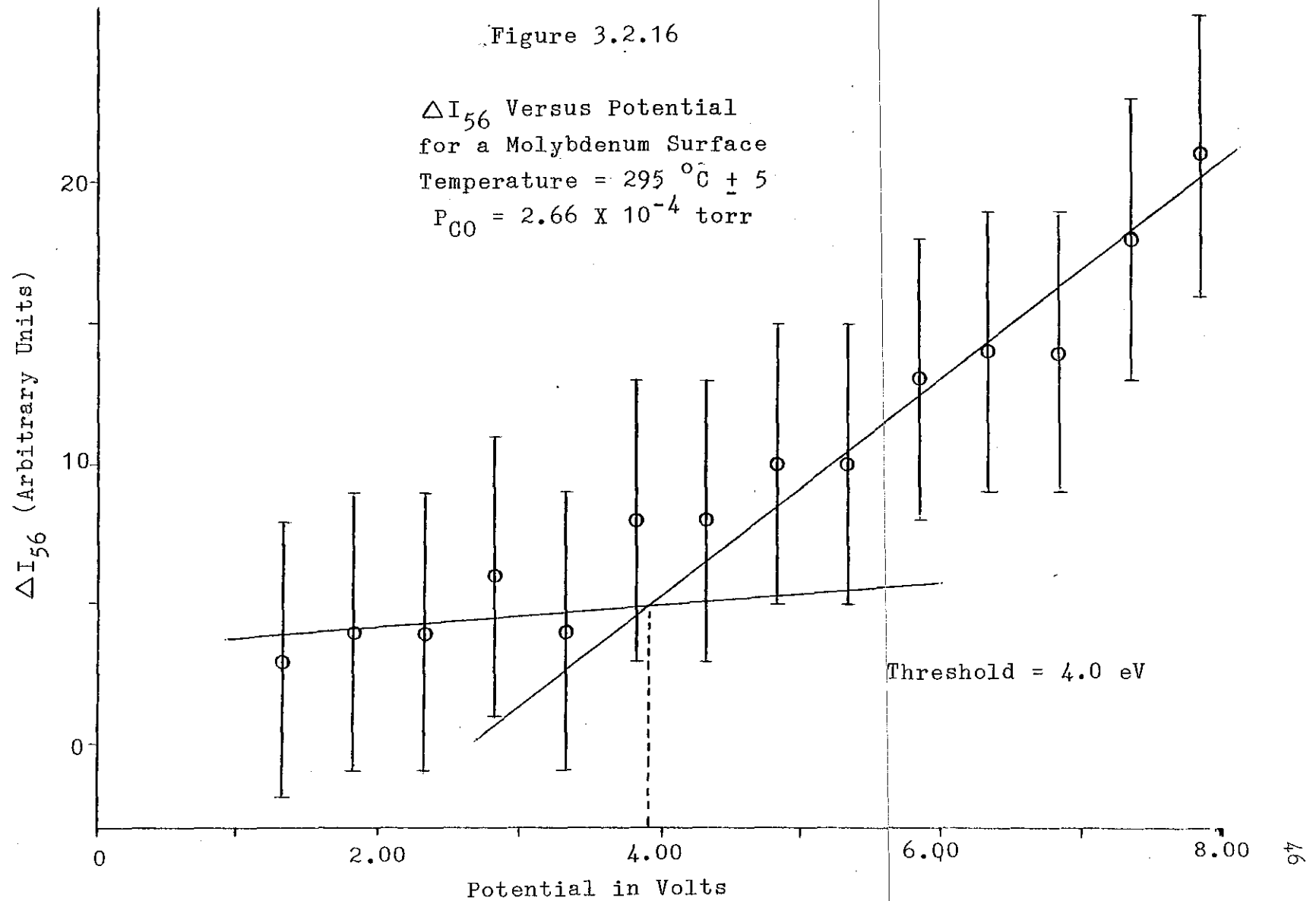


Figure 3.2.17

$\Delta I_{68}$  Versus Potential  
for a Gold Surface  
Temperature =  $115^{\circ}\text{C} \pm 5$   
 $P_{\text{CO}} = 2.66 \times 10^{-4}$  torr

$\Delta I_{68}$  (Arbitrary Units)

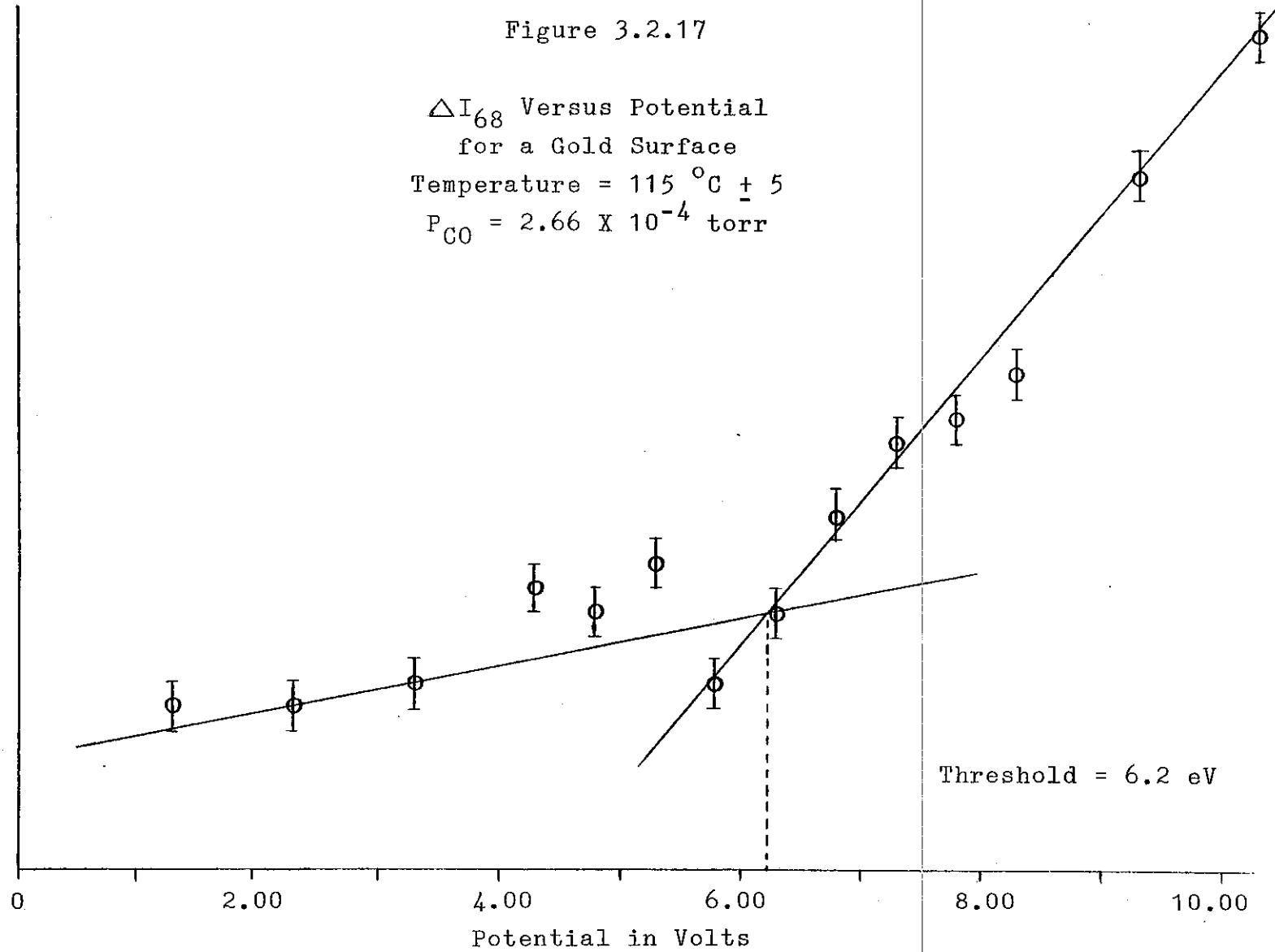


Figure 3.2.18

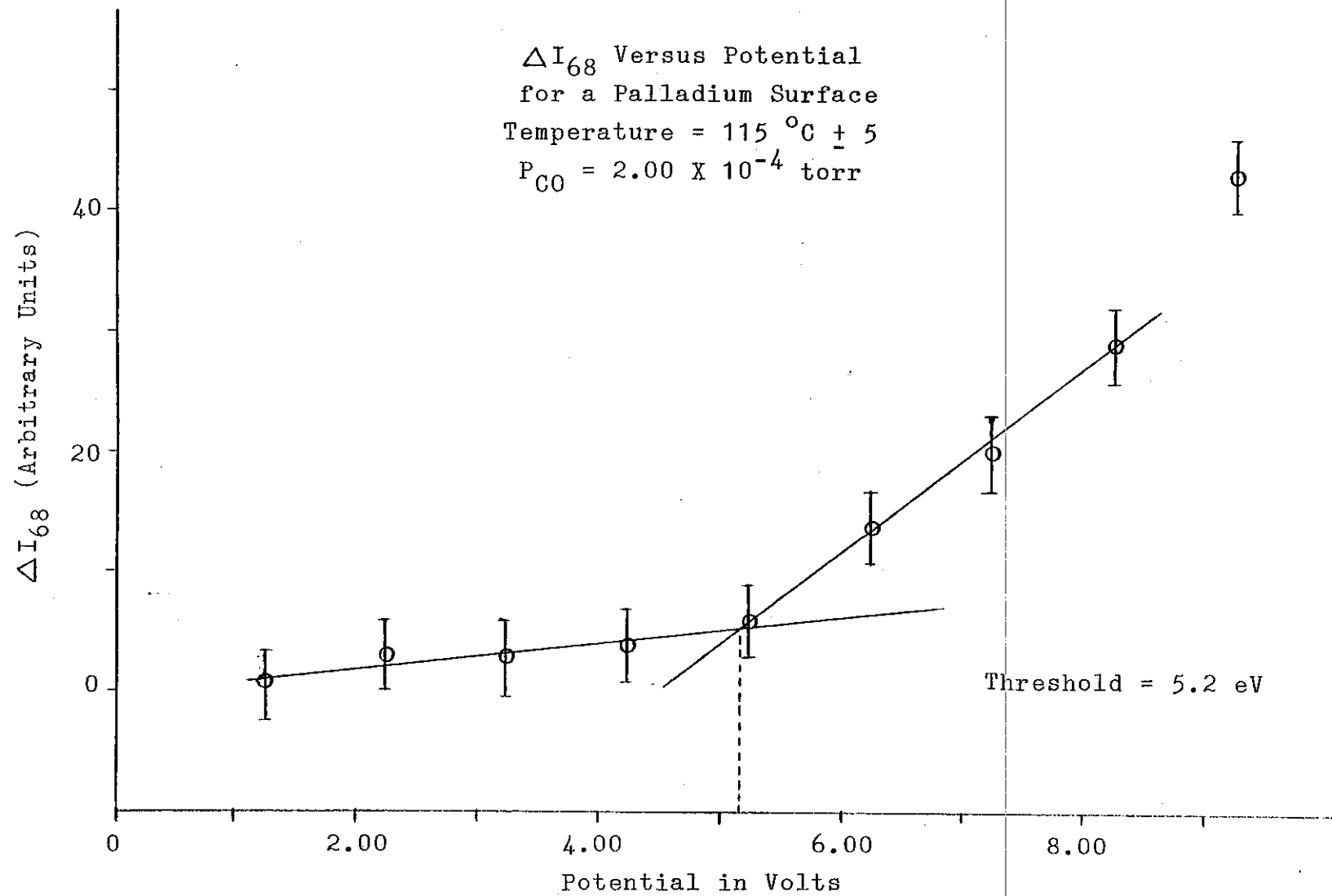


Figure 3.2.19

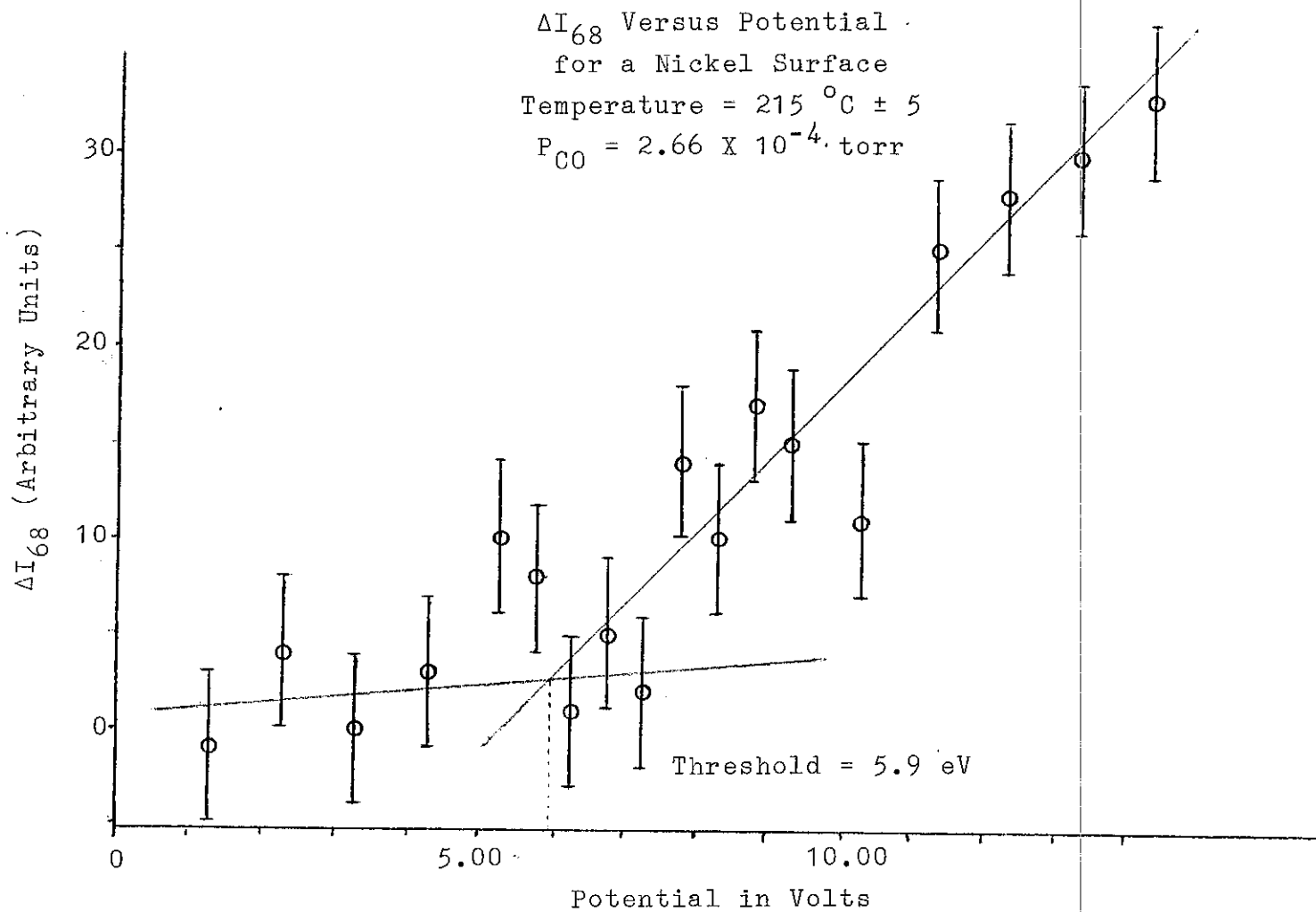




Figure 3.2.20

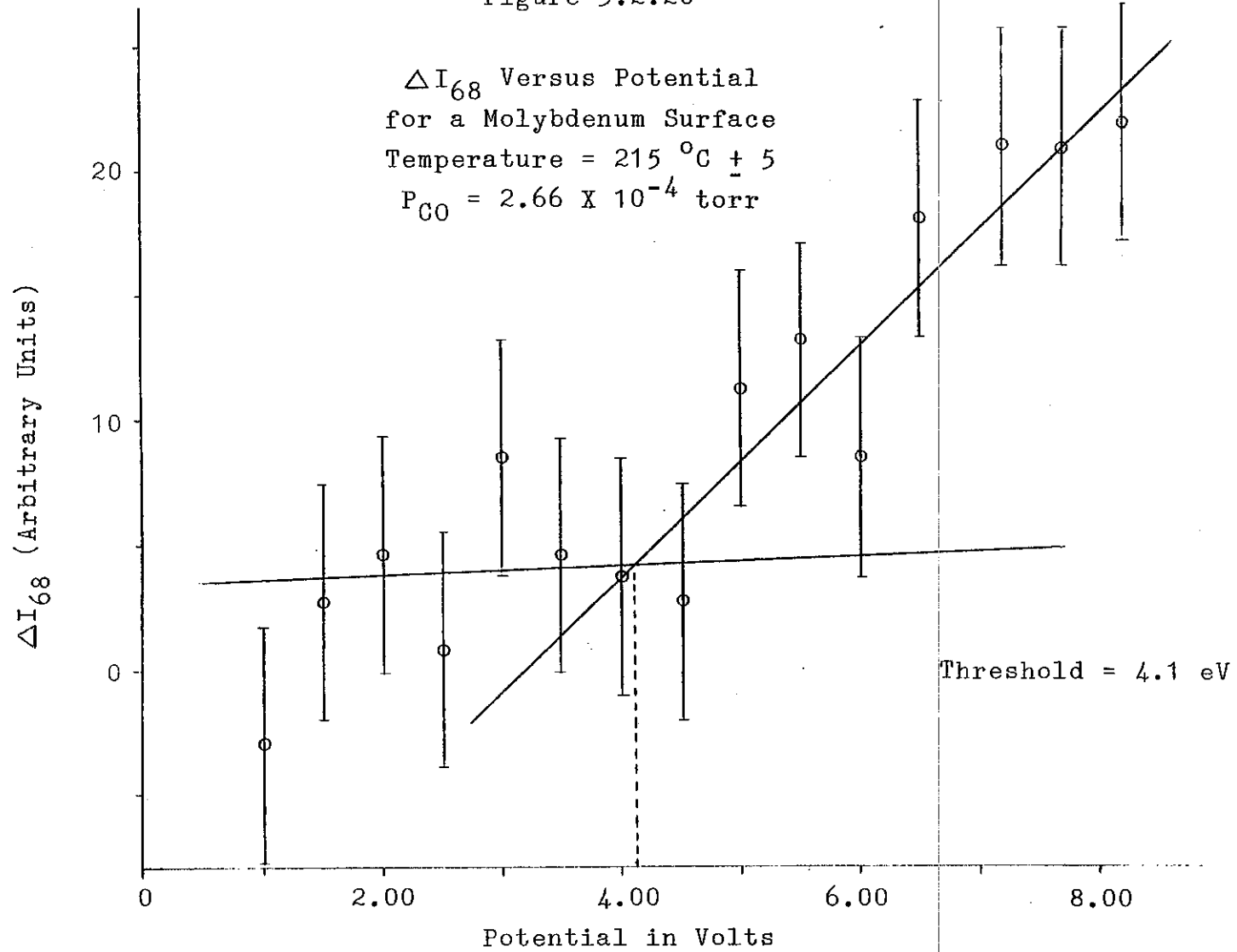


Table 3.2.2

Threshold Values (in Electron Volts)  
for Various Metal Surfaces at  
44, 56 and 68 amu<sup>a</sup>

Surface	Mass Level:			
	44	56	68	Average
Gold	5.9	5.8	6.2	6.0
Palladium	4.9	4.4 <sup>b</sup>	5.2	4.8
Nickel	5.7	6.6	5.9	6.1
		6.3 <sup>b</sup>		
Molybdenum	3.8	4.0 <sup>c</sup>	4.1	4.1
Tungsten	3.0			3.0

a. Temperature is 115 °C ± 5 unless otherwise indicated.

b. Temperature = 215 °C ± 5.

c. Temperature = 295 °C ± 5.

3.3.3. It was not possible to do this for mass levels 40, 56 and 68 because of the small changes involved. Instead,  $\Delta I_x$  was measured as a function of pressure where the potential was incremented between 0.0 and 8.0 V as explained in the experimental section.

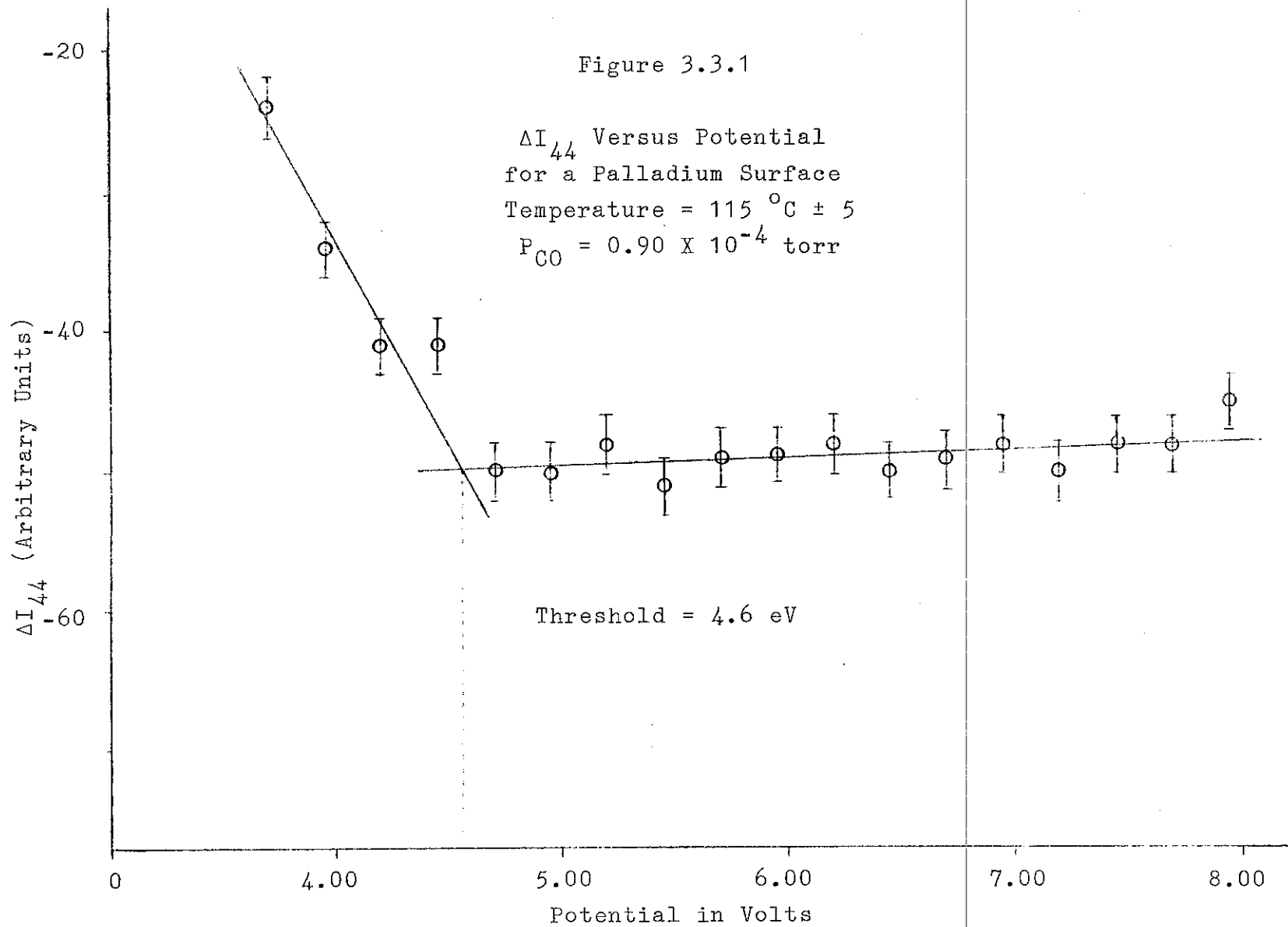
As shown in Figures 3.3.1 through 3.3.3, the threshold stays constant with increasing pressure within experimental error. The decrease in  $\Delta I_{44}$  becomes more pronounced with increasing pressure and the threshold is more defined. The thresholds determined at the three pressures are:

<u>Pressure(<math>\times 10^4</math> torr)</u>	<u>Threshold(eV)</u>
0.90	4.6
1.62	4.9
2.30	4.8

More weight should be given to the values obtained at the higher pressures.

In the remaining graphs in this section,  $\Delta I_x$  was measured while incrementing the potential between 0.0 and 8.0 V at several pressures. The pressure was measured via the Vac Ion gauge and is therefore in microamps. To obtain a rough idea of the actual pressure within the reaction vessel, refer to Figure 2.3.1.2.

Figure 3.3.4 illustrates the pressure dependence for mass level 44. The change is negative with applied potential, which may be implied from the previous discussion, and increases in magnitude with increasing pressure. Two plateaus are discernible. One plateau occurs between 15 and 20  $\mu\text{A}$  while the other occurs between 35 and 40  $\mu\text{A}$ . These



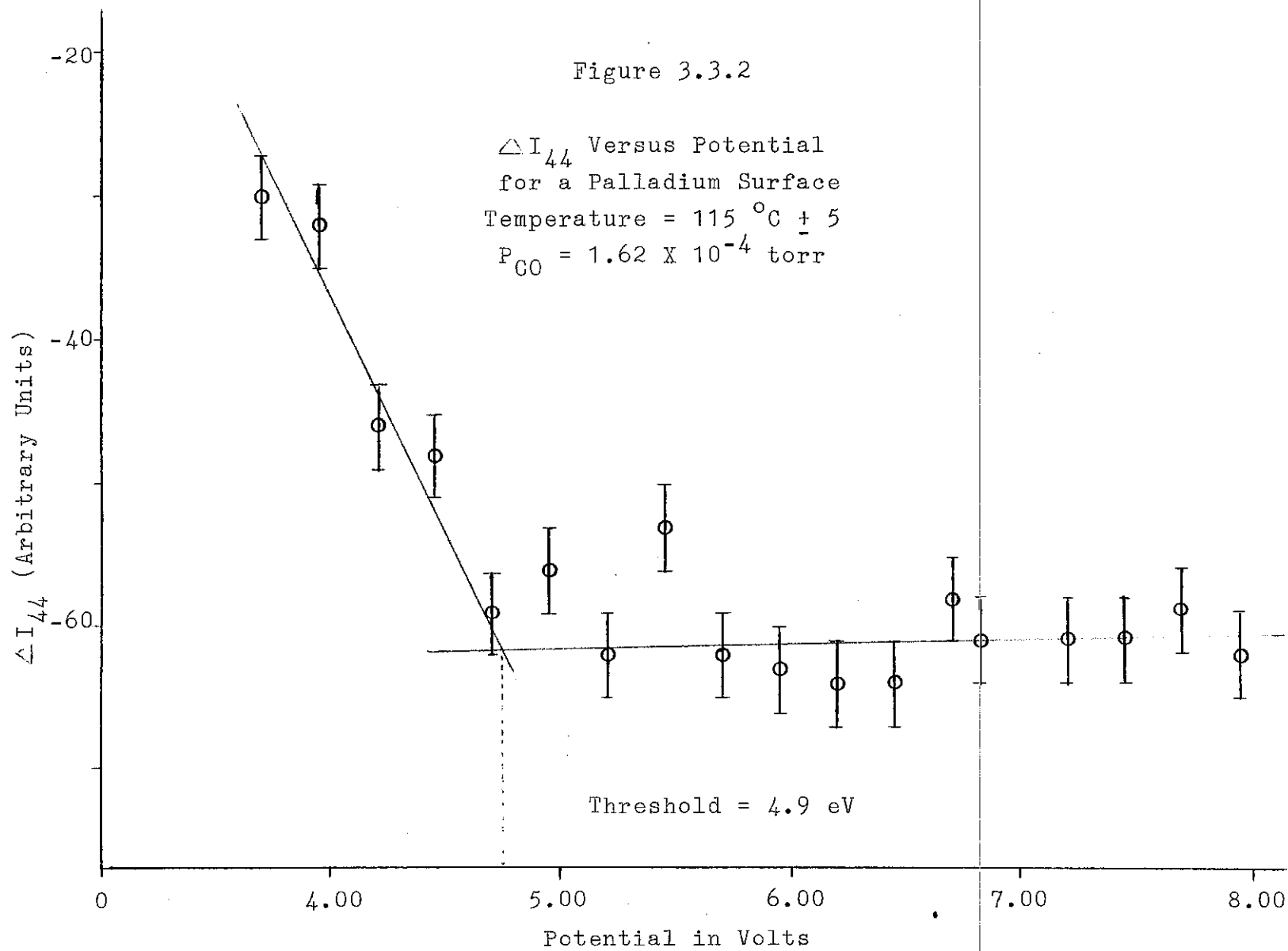


Figure 3.3.3

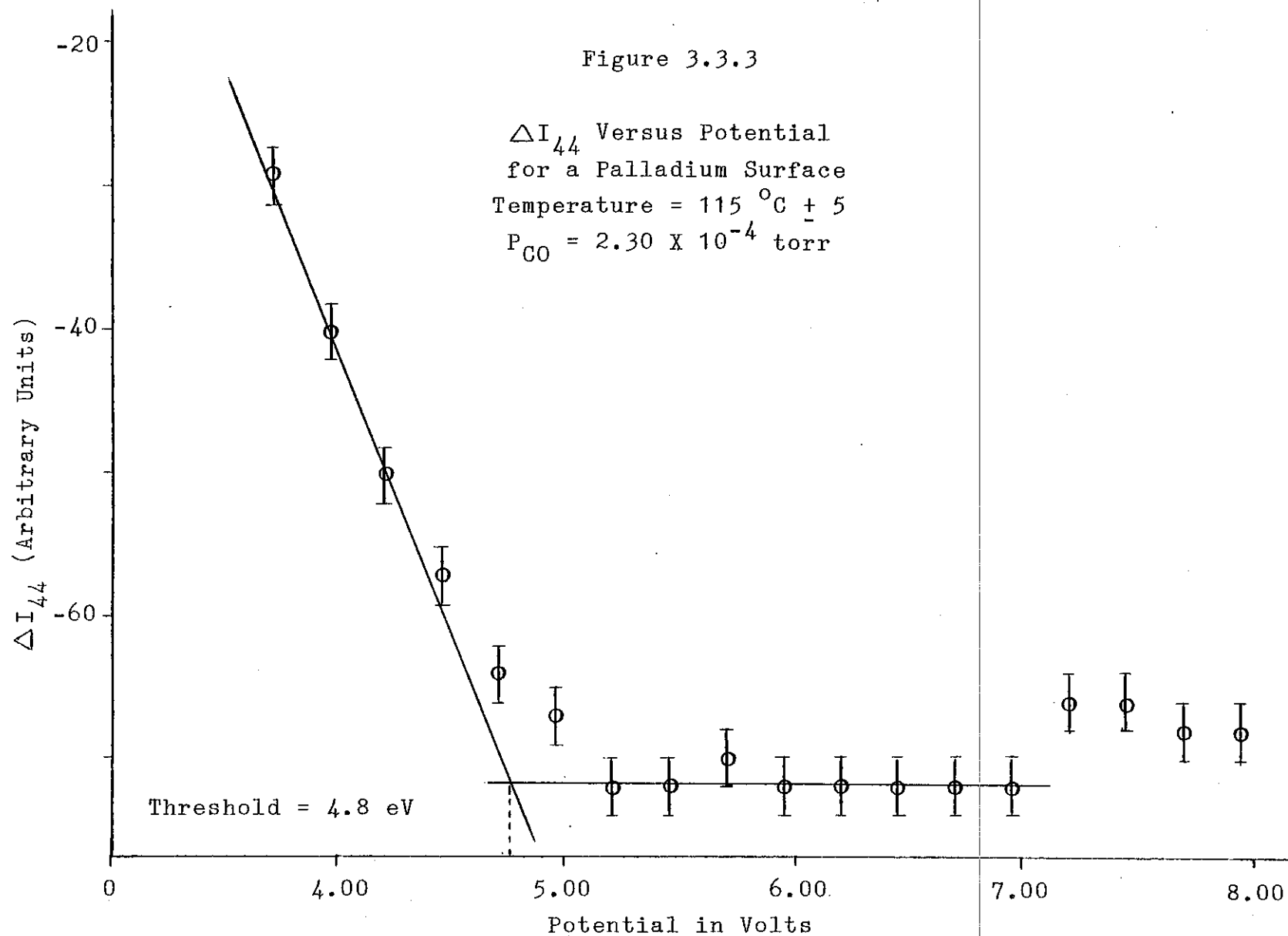
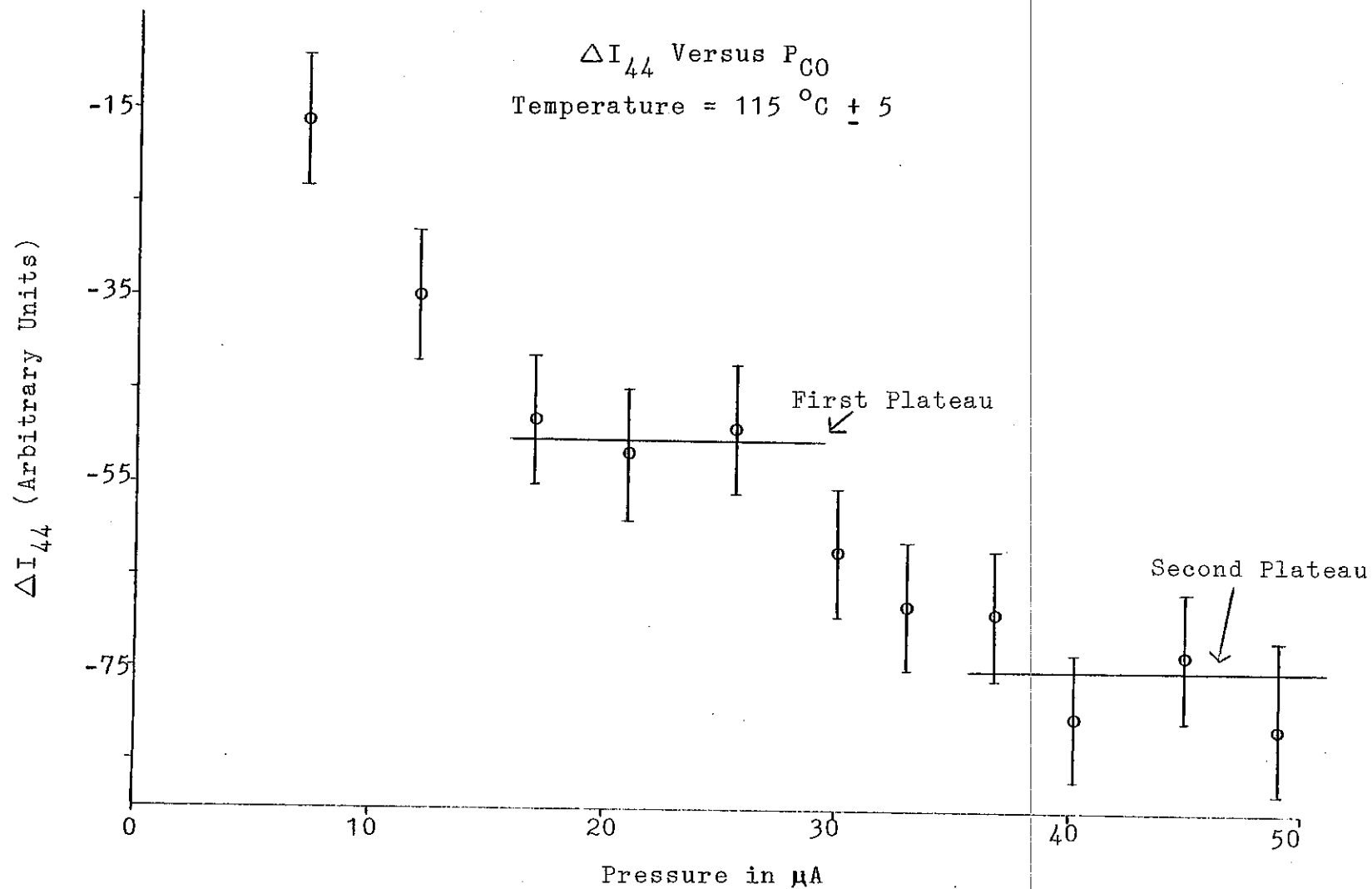


Figure 3.3.4



plateaus correspond roughly with peaks and plateaus which occurred at other mass levels as shown in Figures 3.3.5 through 3.3.9. The positions of these peaks and plateaus have been tabulated in Table 3.3.1. The agreement is not good, but it should be remembered that the Vac Ion gauge is not a good source for measuring the reaction vessel pressure from day to day. The shapes of the curves are similar enough to imply that they are all involved in the same process. Increasing the temperature for 56 and 68 amu greatly increased  $\Delta I_x$ . For this reason, Figures 3.3.7 and 3.3.9 should be given particular attention. When these are compared with Figure 3.3.4, a clear trend can be seen.

### 3.4 Effect of Oxygen

The effect of oxygen on the behavior of  $\Delta I_{44}$  as a function of potential was determined. This was done for palladium and gold surfaces by first treating the surface with oxygen and observing  $\Delta I_{44}$  over the range of 0.00 to 40.0 V. The surface was then treated with hydrogen and  $\Delta I_{44}$  was observed over the same range of potential. Figures 3.4.1 and 3.4.2 illustrate the results.

In both cases,  $\Delta I_{44}$  was more positive after treatment with oxygen than with hydrogen. Also, the cross over point when  $\Delta I_{44}$  again becomes positive was shifted to a lower potential and the positive change in  $\Delta I_{44}$  became more pronounced at the higher potentials.



Figure 3.3.5

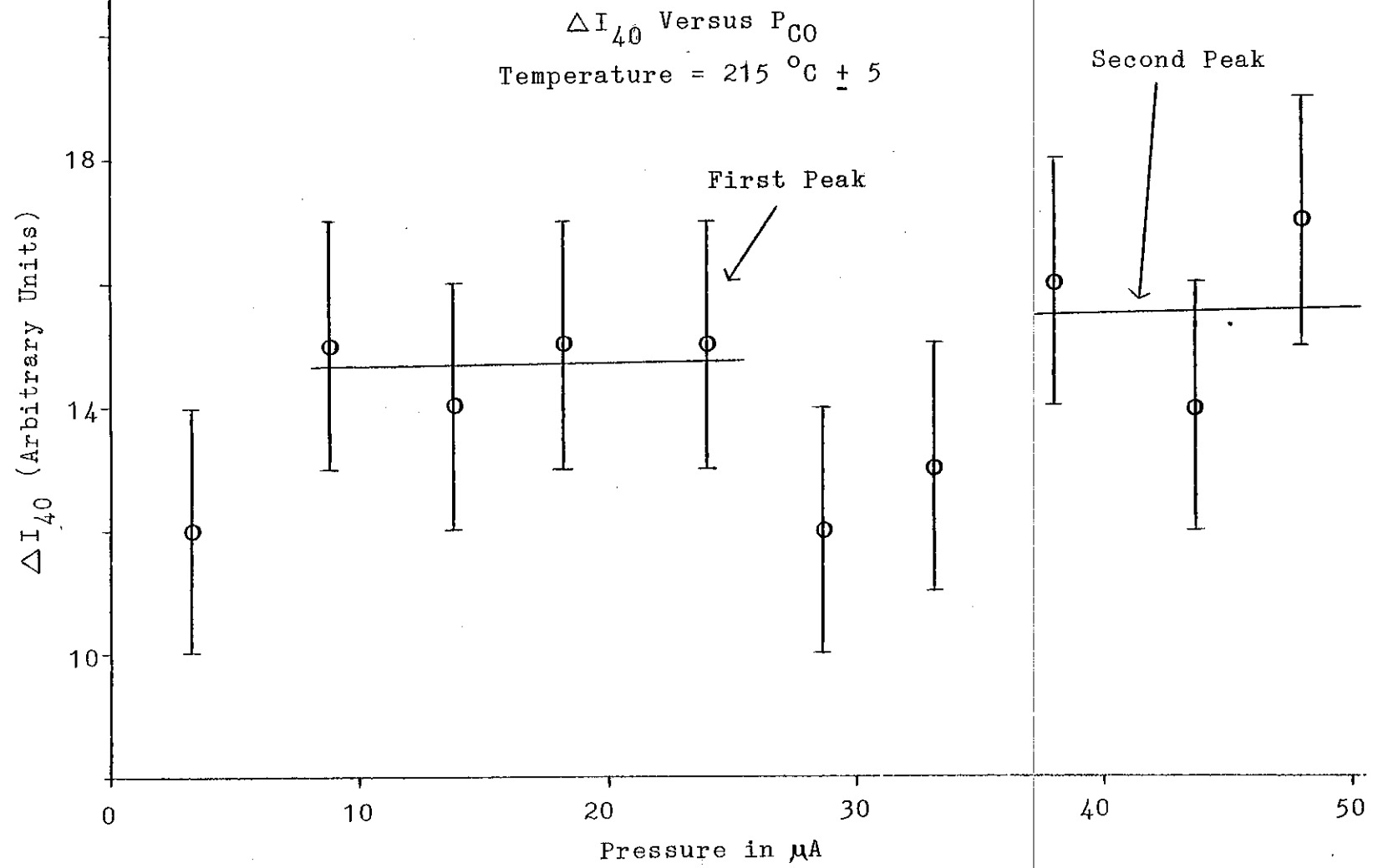


Figure 3.3.6

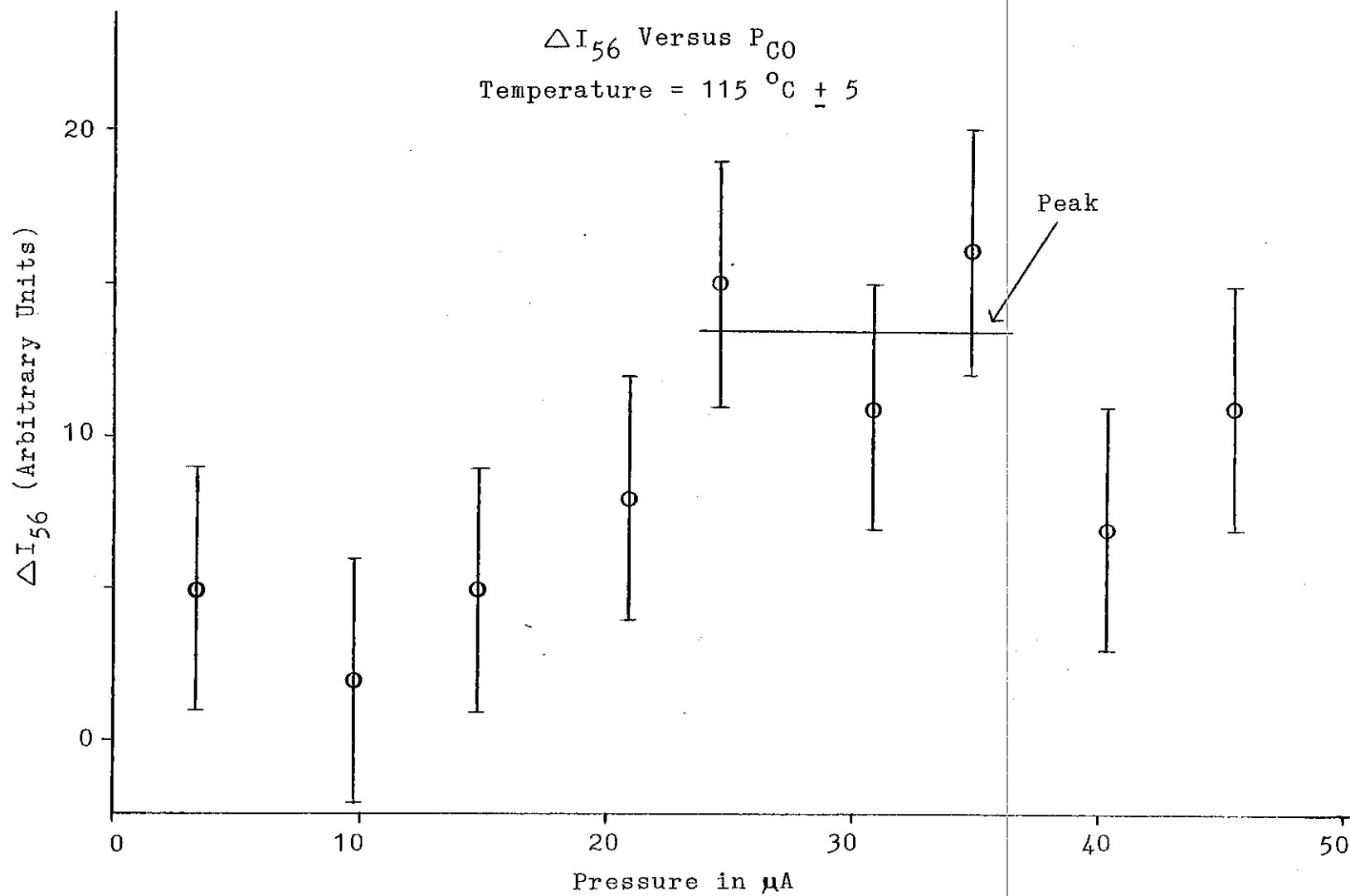


Figure 3.3.7

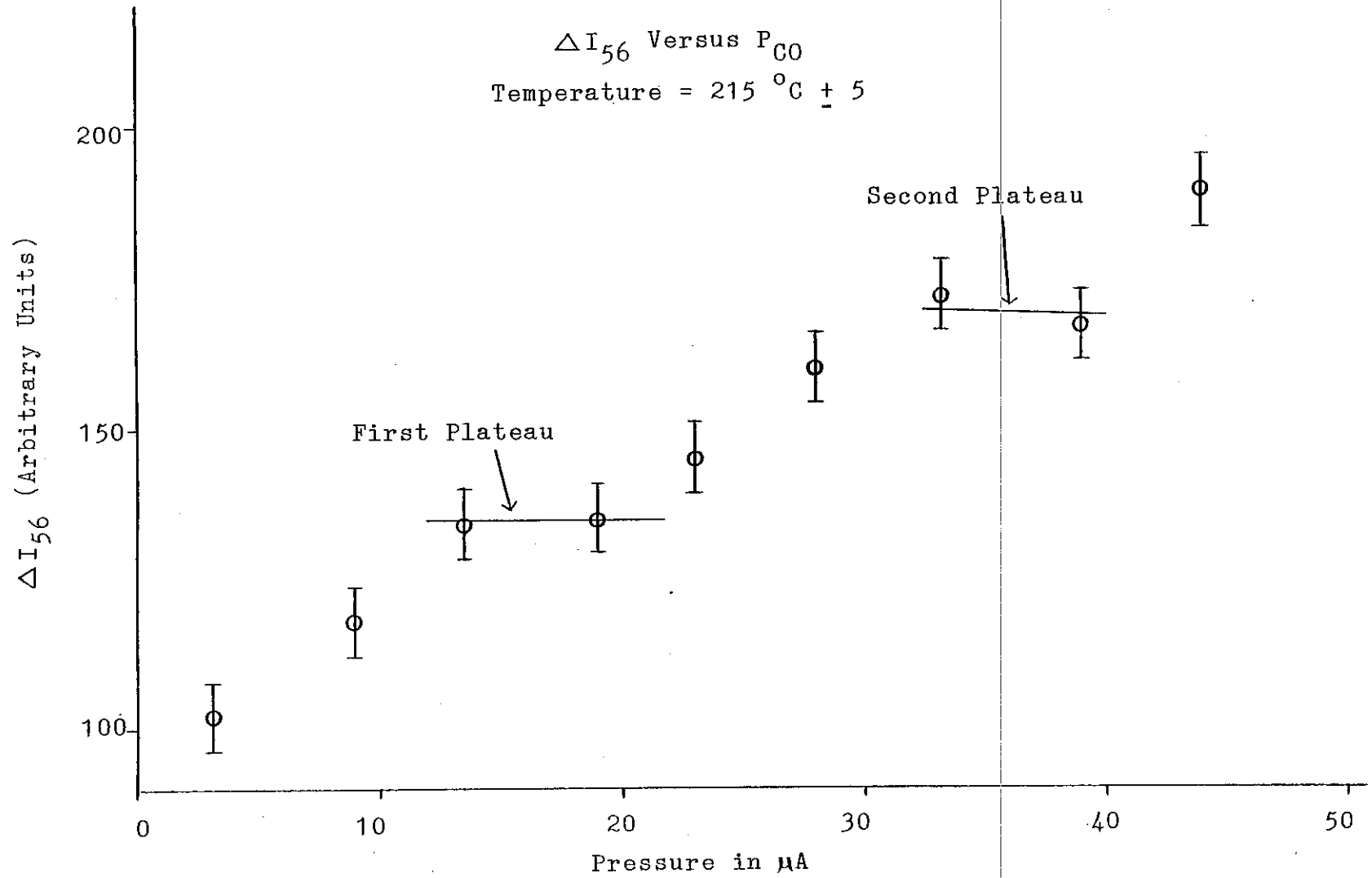


Figure 3.3.8

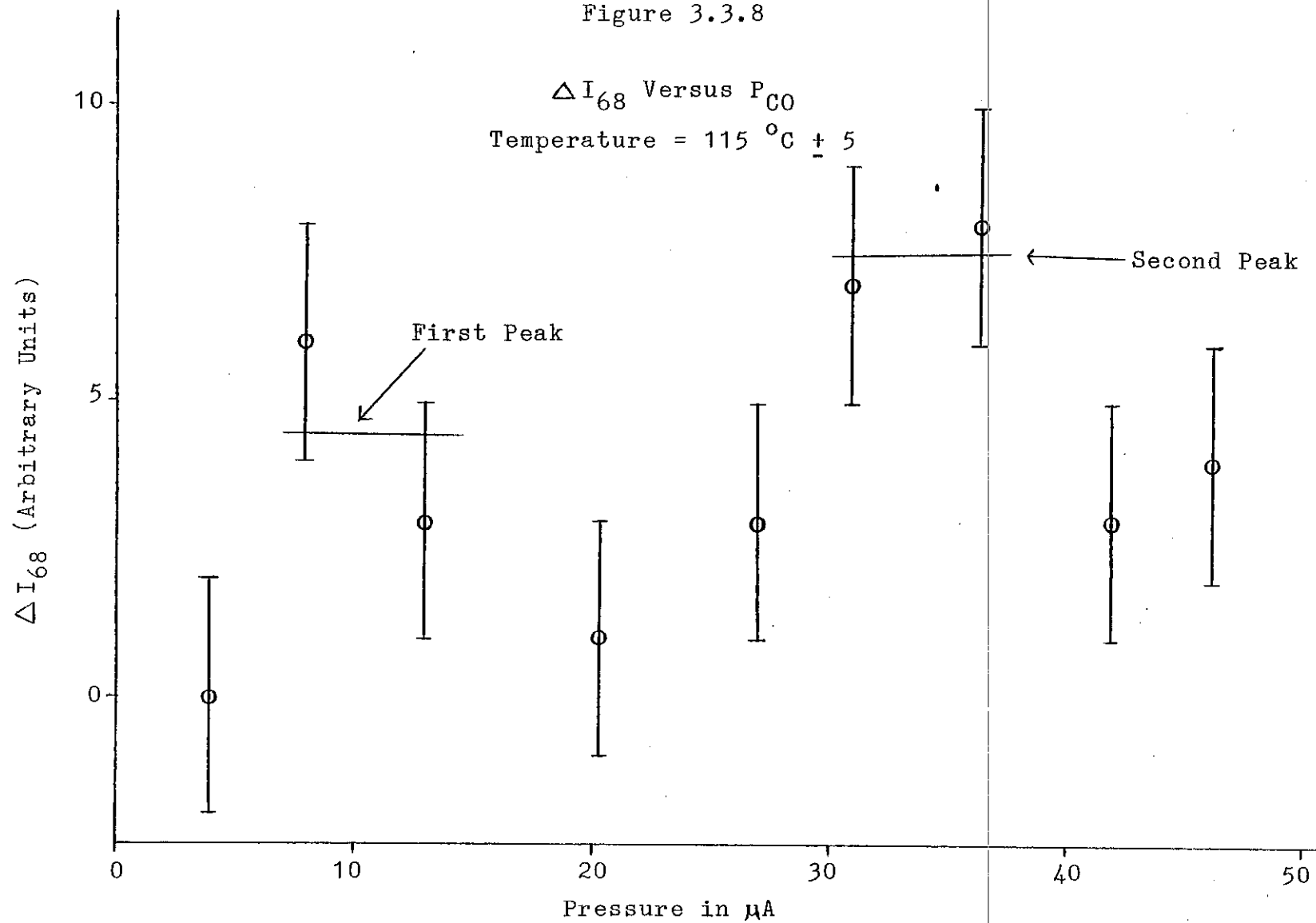


Figure 3.3.9

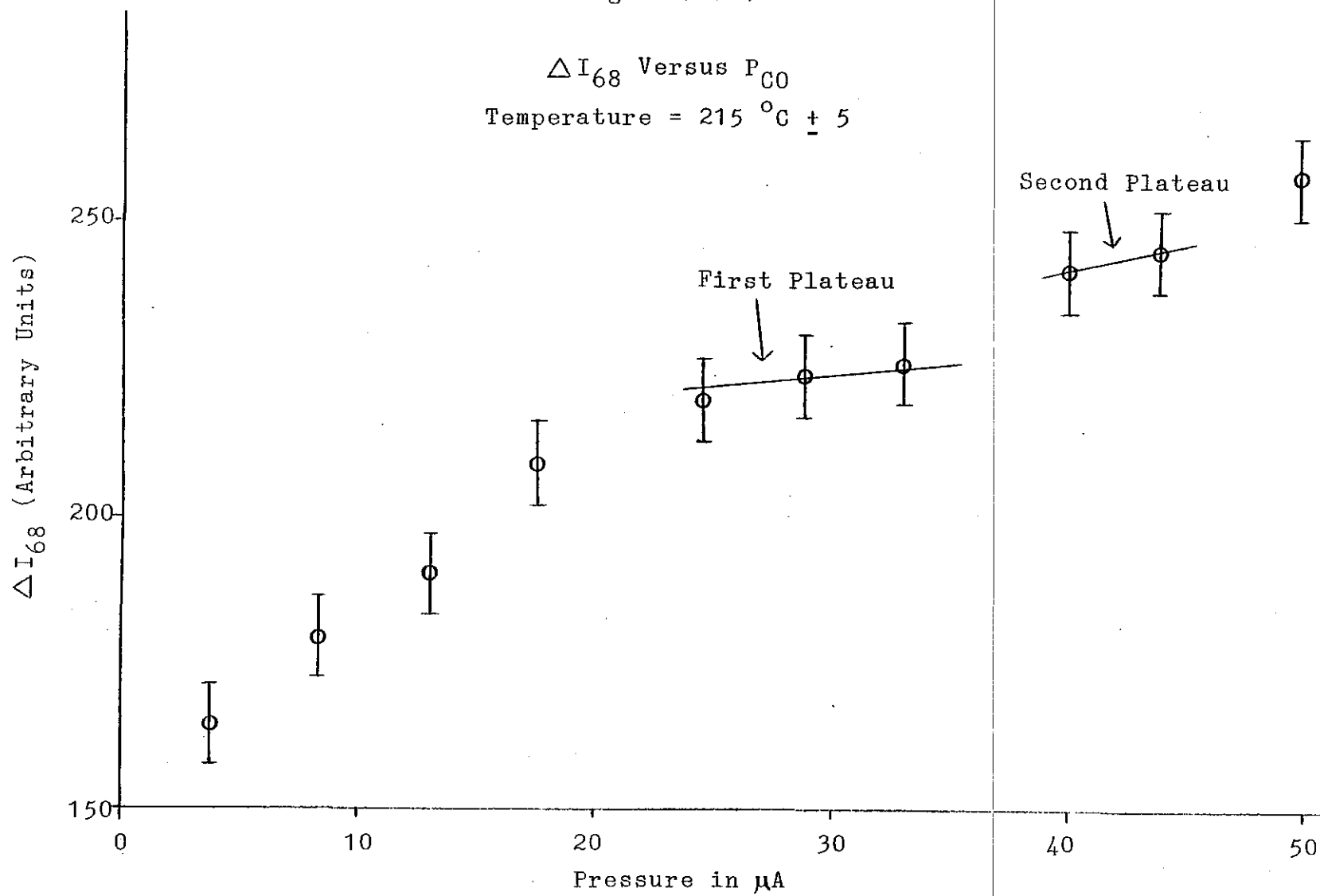


Table 3.3.1

Position of Peaks and  
Plateaus for  $\Delta I_x$  for  
Mass Levels 40, 44, 56 and 68

Mass Level	Temperature ( $\pm 5^\circ\text{C}$ )	Position of First Plateau or Peak ( $\mu\text{A}$ )	Position of Second Plateau or Peak ( $\mu\text{A}$ )
40	215	9-23	48-50
44	115	17-26	40-50
56	115	23-34	---
56	215	12-22	32-43
68	115	9-16	30-38
68	215	23-34	40-48

Figure 3.4.1

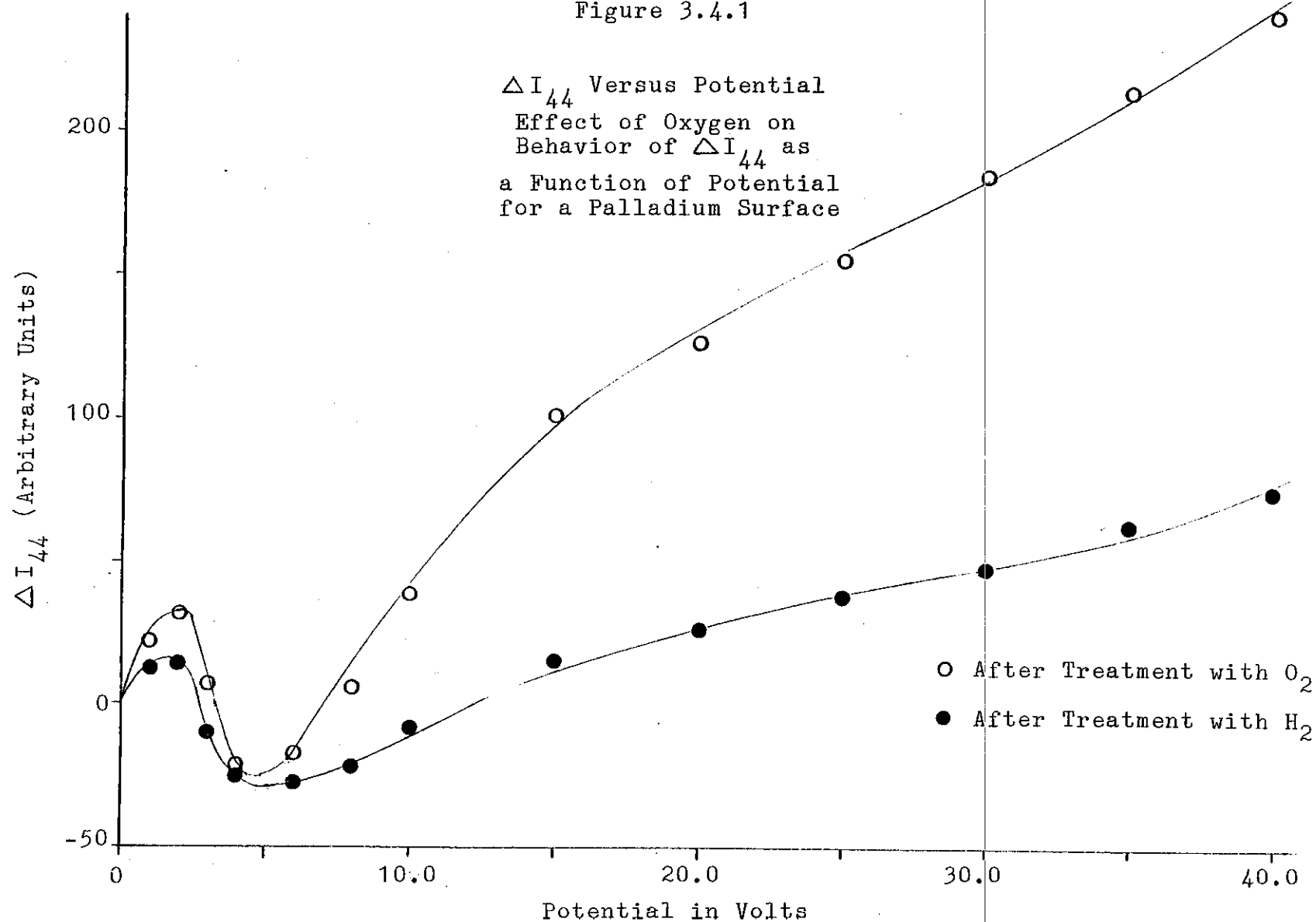
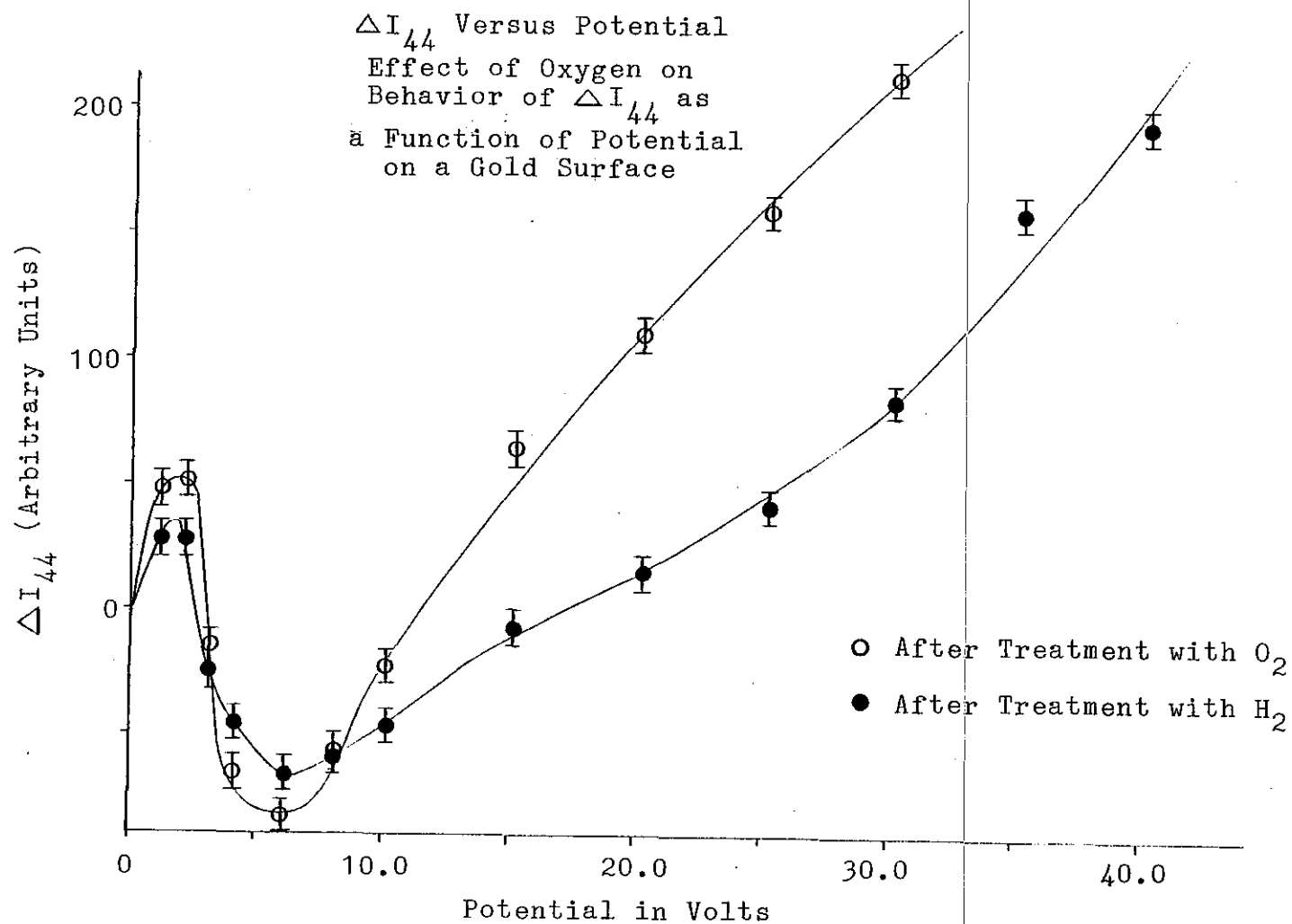


Figure 3.4.2





## Chapter 4

### Discussion

#### 4.1 Relation of Threshold Potentials to Heats of Adsorption

The energy necessary to excite  $\text{CO}(X^1\Sigma^+)$  to  $\text{CO}(a^3\Pi)$  has been reported as 6.3 eV in the gas phase via electron impact.<sup>9</sup> The average threshold potentials ( $E_{th}$ ) reported in Table 3.2.2 have been subtracted from this value and the differences ( $E_{diff}$ ) are given in Table 4.1.1. Also shown are the  $E_{th}$  values and the heats of adsorption ( $E_{ads}$ ) for CO adsorbed on the metal surfaces studied in this dissertation.

There is good agreement between the differences reported and the  $E_{ads}$  values given implying a relationship between  $E_{th}$  and  $E_{ads}$ . It is widely accepted that the metal-carbon (M-C) bond for surface bound carbon monoxide is caused by sigma ( $\sigma$ ) donation from the nonbonding orbital on the carbon (containing one pair of electrons) to the metal in conjunction with pi ( $\pi$ ) back bonding of electron density from the metal to the empty  $\pi^*$  (antibonding) orbital of CO. The  $d\pi \rightarrow p\pi^*$  back bonding would be expected to weaken the  $\text{C}\equiv\text{O}$  bond and infrared studies show that this is the case.<sup>14</sup> Because of studies such as these,  $\pi$  back bonding is believed to be more important than  $\sigma$  bonding. In fact, the heat of adsorption has recently been calculated to be a function of the degree of back bonding to the carbonyl.<sup>15,16</sup>

If this is the case, the energy of the  $\pi^*$  orbital

Table 4.1.1

Relationship Between  $E_{th}$  and  $E_{ads}$   
for the Surfaces Studied  
(Values in Electron Volts)

Surface	$E_{th}$	$E_{diff}$	$E_{ads}$
Gold	6.0	0.3	0.39 <sup>a</sup>
Palladium	4.8	1.5	1.57 <sup>b</sup>
Nickel	6.1	0.2	1.25 <sup>c</sup>
Molybdenum	4.1	2.2	2.60 <sup>d</sup>
Tungsten	3.0	3.3	3.47 <sup>d</sup>

a. See reference 10

b. See reference 11.  $E_{ads}$  was determined for a wide variety of palladium surfaces. The values did not vary more than 8.0%. The value shown above is an average of these values.

c. See reference 12.  $E_{ads}$  was determined for three nickel surfaces. The values varied less than 10%. The value shown above is an average of these values.

d. See reference 13.

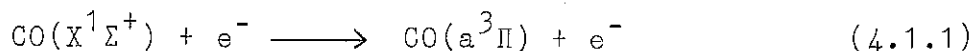
would be stabilized by approximately  $E_{\text{ads}}$  and the energy of excitation ( $n \rightarrow \pi^*$ ) would be reduced by this amount.

Further support comes from a threshold potential reported by Menzel of 5 eV for desorption of CO from tungsten.<sup>17</sup>

He attributed this to transition of an electron from the M-C bond to a vibrationally excited higher electronic state followed by subsequent desorption of  $\text{CO}^*(\text{g})$ . This work supports this conclusion with the exception that metastable surface bound states must also be possible. That is, adsorbed excited-state species must exist at least long enough to enter into the proposed subsequent reactions.

Because the surfaces studied were non-uniform in nature, it is difficult to draw specific conclusions about their relative activities. However, some general conclusions may be drawn. Molybdenum was by far the least active of the metals studied with the exception of tungsten. The low activity of tungsten precluded the observation of products at 56 and 68 amu. CO is known to disproportionate on group VI transition metal surfaces. In our work this is strongly evidenced by the high desorption peak for  $\text{CO}_2$  shown in Figure 3.2.5 between 1.0 and 3.0 eV. Gold was found to be quite active and measurements of  $\Delta I_x$  values were the easiest to obtain. These results may be explained by considering the effect which chemisorption has on the excitation cross section ( $\sigma_{\text{ads}}$ ) of CO.

In the gas phase, the excitation cross section for the following transition is greater than  $10^{-18} \text{ cm}^2$ :



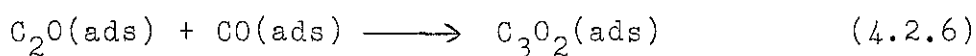
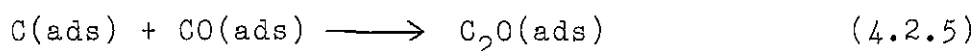
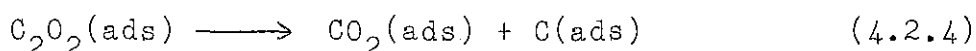
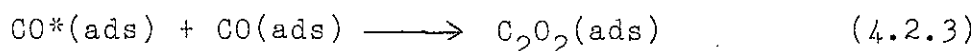
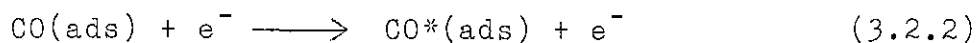
It might be expected that the cross section in the adsorbed state would be just as high. However, Menzel has reported cross sections of  $3 \times 10^{-18}$  to  $3 \times 10^{-21} \text{ cm}^2$ , depending on the state of the adsorbed CO, for CO adsorbed on a tungsten surface.<sup>18</sup> He attributed this to a rapid filling of the electron vacancy left after excitation by transfer of an ~~electron from the metal reservoir.~~ Menzel further pointed out that  $\sigma_{\text{ads}}$  is directly related to the M-C bond strength. The stronger the bond, the lower the cross section as revealed by cross sections for the various states of CO adsorbed on tungsten.<sup>17</sup>

If  $E_{\text{ads}}$  is a measure of the M-C bond strength,<sup>19</sup> and if the excited-state quenching, discussed above, depends on this bond strength, the cross section would be expected to increase as  $E_{\text{ads}}$  decreases. In our studies, molybdenum was the least active while gold was most active.

No definite explanation for the high  $E_{\text{th}}$  value of nickel can be offered at this time. It may be that back bonding is less pronounced for nickel since it is in the first transition series and the d orbitals are less diffuse than in the second and third transition series.

#### 4.2 Reaction Mechanism

The proposed reaction sequence of  $\text{CO}(a^3\Pi)$  to form  $\text{CO}_2$  and  $\text{C}_3\text{O}_2$  in the gas phase has been given in equations 1.3 to 1.6. An analogous sequence on a metal surface is:



This is given added support by the photochemistry described earlier of CO adsorbed on a tungsten surface.

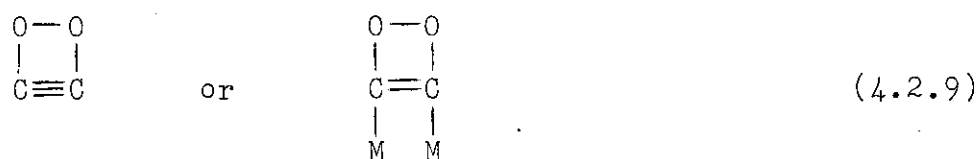
To our knowledge,  $\text{C}_2\text{O}_2$  has not been observed as an intermediate in the gas phase reaction of  $\text{CO}(a^3\Pi)$ . It may be that there are two isomers of  $\text{C}_2\text{O}_2$ . The observed form may have the following structure:



This would be analogous to  $\text{C}_3\text{O}_2$  whose structure is known to be:



The intermediate form may have a completely different structure. For example:



It may be that  $\text{CO}^*(\text{ads})$  is reacting with  $\text{CO(g)}$  in 4.2.3 above. This is unlikely because of the low pressures at which the experiments were conducted. The peaks and plateaus reported in section 2.3 also support the conclusion that the formation of  $\text{C}_2\text{O}_2$  is strictly a surface phenomenon.

### 4.3 Behavior at 44 amu

The behavior at 44 amu deserves some consideration. The peaks observed from 1.0 to 3.0 eV are believed to represent desorption of  $\text{CO}_2$ . We have observed carbon monoxide interacting with the hot thorium oxide coated filament to form carbon dioxide. It is also known to react with oxygen adsorbed on metal surfaces.<sup>20</sup> A steady state of  $\text{CO}_2$  is therefore expected to exist when carbon monoxide gas is passed over the hot filament. Some of this  $\text{CO}_2$  will adsorb on the collector surface. The adsorbed  $\text{CO}_2$  is believed to immediately begin to desorb upon electron bombardment. The decrease in intensity of this peak when the temperature is increased, as shown by Figures 3.2.2 and 3.2.3 for CO adsorbed on a palladium surface, also supports this interpretation.

At some point the positive change starts to become less pronounced and actually becomes negative. The minimum dissociation energy of  $\text{CO}_2$  is 5.8 eV.<sup>21</sup> Therefore, this is unlikely as an explanation, even if surface effects are taken into account. A more likely explanation is that some of the CO molecules are prevented from interacting with the hot filament because of the flux of electrons coming off the filament when a potential is applied.

Eventually the proposed reaction sequence given in section 4.2 is believed to compete with this process and  $\Delta I_{44}$  becomes less negative and begins to become positive at energies above  $E_{th}$  for the excitation of adsorbed CO.

#### 4.4 Conclusion

We believe we have developed a new technique which will, after further refinements, shed a great deal of light on the interaction of gas phase molecules with metal surfaces. The  $E_{th}$  values of mass levels 44, 56 and 68 were explained in terms of  $d\pi \rightarrow p\pi^*$  back bonding from the metal to the carbonyl and the effect this has on stabilizing the  $\pi^*$  orbital of CO. This was interpreted as reducing the energy necessary to excite carbon monoxide relative to the gas phase. This technique may eventually be useful for establishing the relative energy levels of molecular orbitals formed upon interaction of a metal with adsorbate molecules.

## REFERENCES

1. S. Trajmar, Acc. Chem. Res., 1980, 13, 14.
2. L. J. Keiffer, "Bibliography of Low Energy Electron Collision Cross Section Data," National Bureau of Standards Miscellaneous Publication #298, March 10, 1967.
3. G. Liuti, S. Dondes and P. Harteck, J. Chem. Phys., 1980, 44, 4051.
4. G. Ertl and J. Kuppers, "Low Energy Electrons and Surface Chemistry," Verlag Chemie, Weinheim, Germany, 1974, Ch. 9.
5. Ibid., Ch. 2.
6. Ibid., Ch. 3.
7. D. Menzel and R. Gomer, J. Chem. Phys., 1964, 41, 3311.
8. R. A. Marbrow and R. M. Lambert, Surf. Sci., 1977, 67, 489.
9. M. A. Gordon and L. E. Snyder, "Molecules in the Galactic Environment," John Wiley and Sons, New York, 1973, 381.
10. B. M. W. Trapnell, Proc. R. Soc., 1953, A218, 566.
11. H. Conrad, G. Ertl, J. Koch and E. E. Latia, Surf. Sci., 1974, 43, 462.
12. K. Christmann, O. Schober and G. Ertl, J. Chem. Phys., 1974, 60, 4719.
13. D. Brennan and F. H. Hayes, Phil. Trans. R. Soc., 1965 A258, 347.
14. G. Blyholder, J. Phys. Chem., 1975, 79, 756.
15. G. Doyen and G. Ertl, Surf. Sci., 1974, 43, 197.
16. T. B. Grimley in: "Molecular Processes at Solid Surfaces," Eds. E. Drauglis, R. D. Gretz and R. I. Jaffee, McGraw-Hill, New York, 1969, 299.



17. D. Menzel, Angew. Chem. Internat. Edit., 1970, 9, 255.
18. D. Menzel and R. Gomer, J. Chem. Phys., 1964, 41, 3329.
19. C. Chang, Surf. Sci., 1980, 95, L239.
20. G. Ertl and J. Koch, Zeit. fur Physik. Chem. Neue Folge, 1970, 69, 323.
21. H. Okabe, "Photochemistry of Small Molecules," John Wiley and Sons, New York, 1978, 210.
22. L. M. Stephenson, M. Grdina and M. Orfanopoulos, Acc. Chem. Res., 1980, 13, 419.

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23. J. T. Herron and R. E. Huie, "Mass Spectrometric Studies of the Reactions of Singlet Oxygen in the Gas Phase," Annals New York Academy of Sciences, 1969, 171, 229.

## APPENDIX A

### MASS SPECTROMETER/MICROPROCESSOR INTERFACE HARDWARE

The mass spectrometer is a Varian CVA-5 which is based upon a Uthe Technology Incorporated (UTI) 100B quadrupole mass analyzer. The UTI 100B is designed so the mass levels can be scanned via a ramp generator within the control box or can be selected manually by adjusting the appropriate controls on the control box. In addition to this, the mass level can be selected by inputting a voltage from an external source. This is a high impedance input and requires 0 to 3.7 V to cover the mass range of 2 to 311 amu.

A CompuPro microprocessor was chosen from Godbout Electronics. This is a S-100 system based upon Godbout's CompuPro "CPU-Z" microprocessor board which is designed around Intel's Z-80 microprocessor chip. The S-100 system is attractive because it is oriented around a 100 pin motherboard which has been designed for mechanical and electrical compatability with the IEEE S-100 bus standard. It provides for ready expansion and updating. Support boards chosen from Godbout's selection were two CompuPro "RAM XX" memory boards (for a total of 64 kilobytes of static RAM), one CompuPro "Interfacer II" board, one CompuPro "System Support 1" board, one CompuPro "Disk 1" disk control board and one CompuPro "Spectrum Board" for graphics capability. The entire system

is operated from a Hazeltine 1420 terminal under CP/M control (trademark for Digital Research's microprocessor operating system). An Epson MX-80 printer was used to generate hard copy.

The interface hardware naturally falls into two categories; one digital to analogue (D/A) converter to set the mass level and one analogue to digital (A/D) converter to read the ion current. Two parallel ports on the Interfacer II board were involved in the interface. Each parallel port has eight lines in and eight lines out for a total of sixteen lines each way. The interval timer was programmed to provide pulses at intervals which could be set under software control in order to provide a way to strobe the A/D converter.

A sixteen bit D/A converter from Analogue Devices (stock number DAC1136 K1111) came as a 44 pin card mounted assembly. It requires a sixteen bit binary input, a strobe to tell it when to begin a conversion and +15 V, -15 V and +5 V power connections. The converter was configured for 0 to 5 V output and the digital and analogue grounds were tied together. Since the mass spectrometer requires a 0 to 3.7 V input, the converter provides accuracy of better than 1 part in 48,000 parts. A factory mounted assembly was chosen to avoid static problems which might be encountered if the converter were hand wired (1 LSB = 72  $\mu$ V). Connection to the two ports on the Interfacer II board is via two standard 26 pin connector cables as shown in figure A.1. The low byte port is configured so that writing to it causes the attention



line to pulse causing the information in both ports to be strobed into the converter. This necessitates writing to the high order byte port first.

A twelve bit A/D converter from Analogue Devices (stock number AD572) was configured to receive 0 to 10 V as shown in Figure A.2. It was mounted on a standard 44 pin connector card. Connection to the two ports on the Interfacer II board is via the same two 26 pin connector cables used with the D/A converter. This is shown in Figure A.3. The standard operation of this assembly is as follows:

1. The interval timer pulses causing the A/D converter to begin a conversion.
2. The status line from the A/D converter goes high causing the sample and hold chip to go into hold mode. This also goes to the input strobe line of both ports.
3. Upon completion of a conversion, the status line goes low causing the sample and hold chip to go into sample mode and causing the new data to be strobed into the two ports.

The Interfacer II board has a control port which has a status bit associated with each of the parallel ports. When data is strobed into the ports, the status bits are set. The computer can monitor this by reading the control port and checking the status bit. A timing diagram is provided in Figure A.4 to illustrate the above procedure.

Figure A.2

Wiring Diagram for 12  
Bit A/D Converter

Letters are pin  
designations(44 pin bus)

W = +5 V  
X = +15 V  
Y = -15 V  
Z = Digital and  
Analogue ground

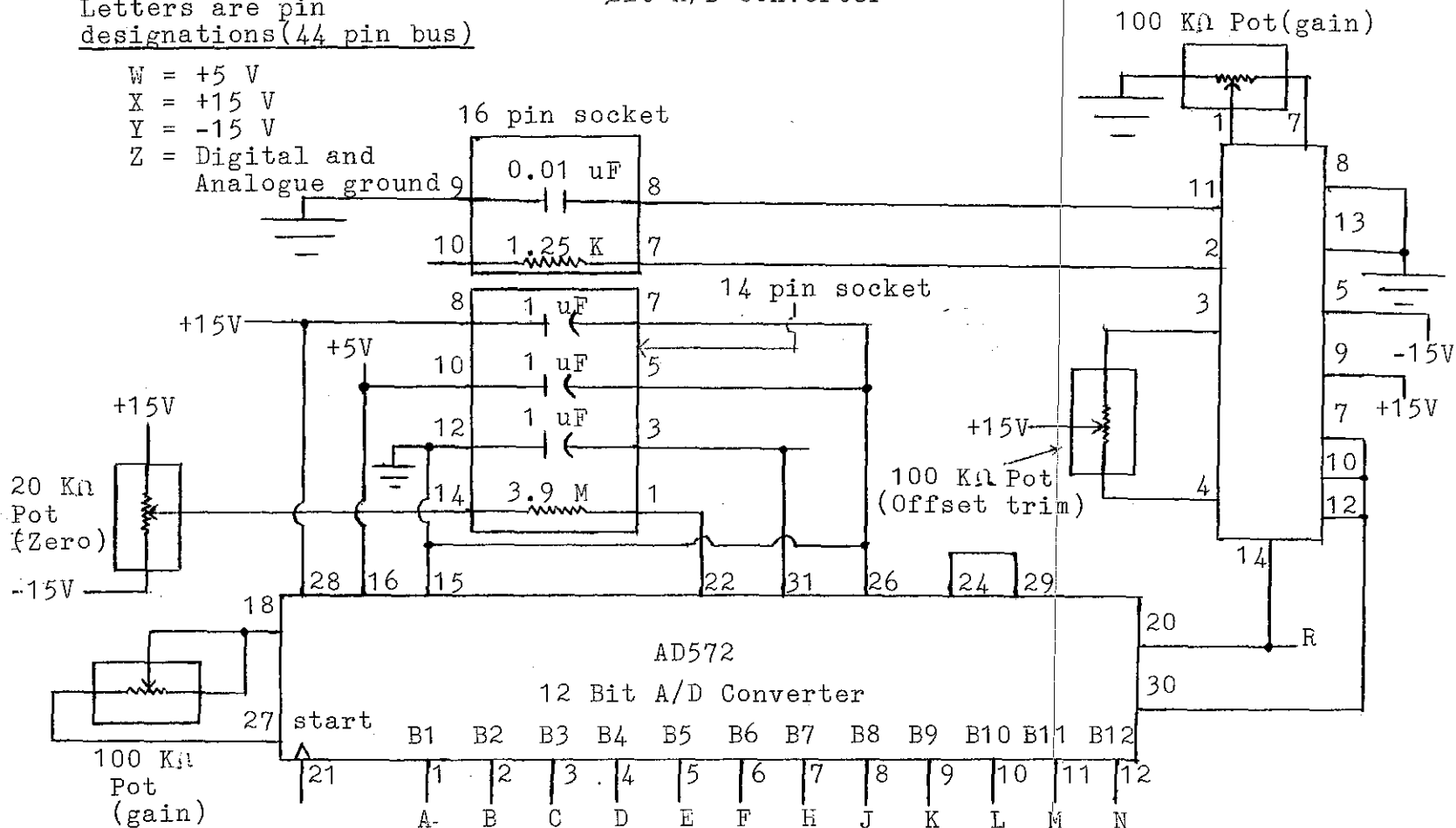


Figure A.3

Interface Between 12 Bit  
A/D Converter and  
Microprocessor

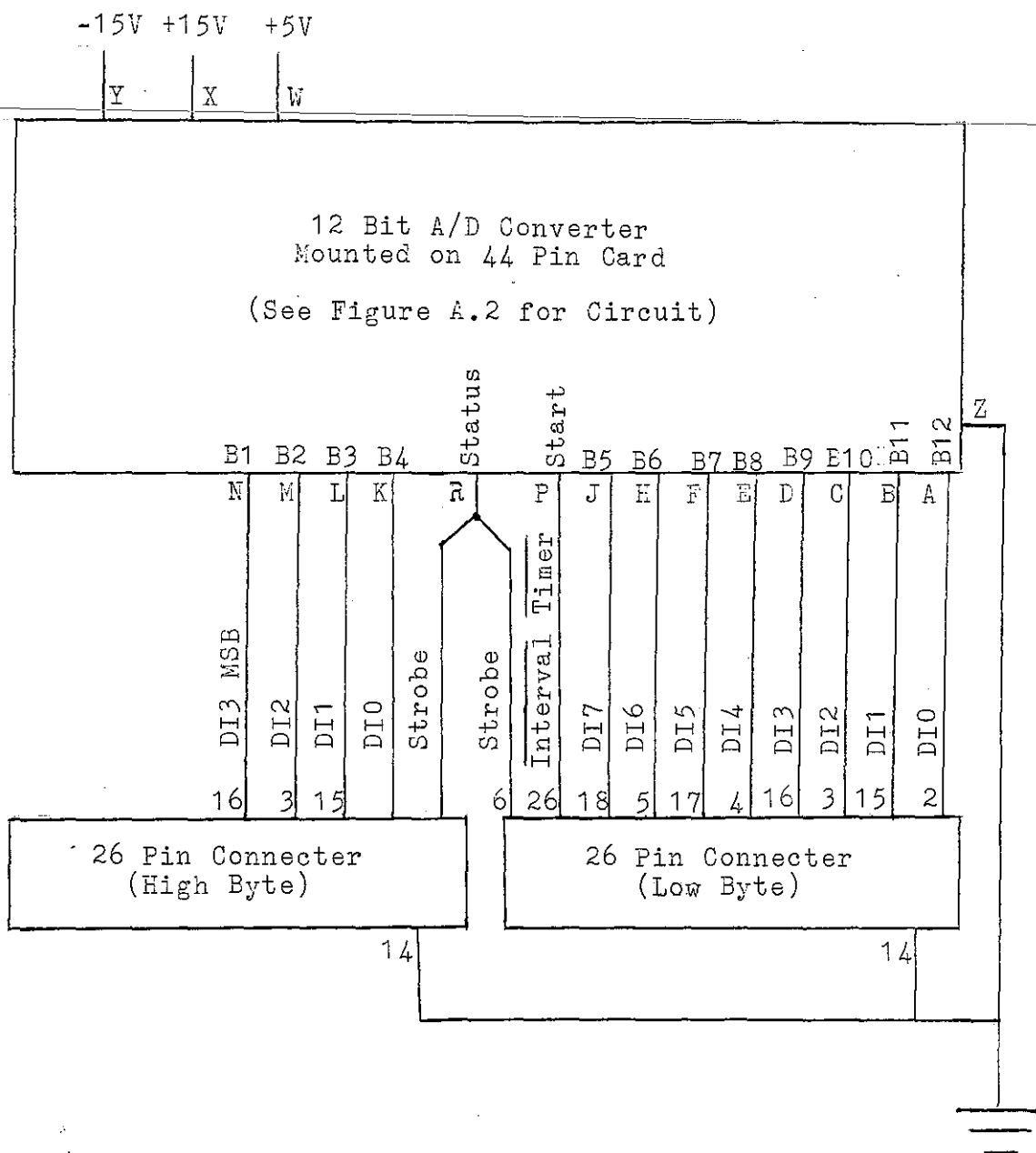
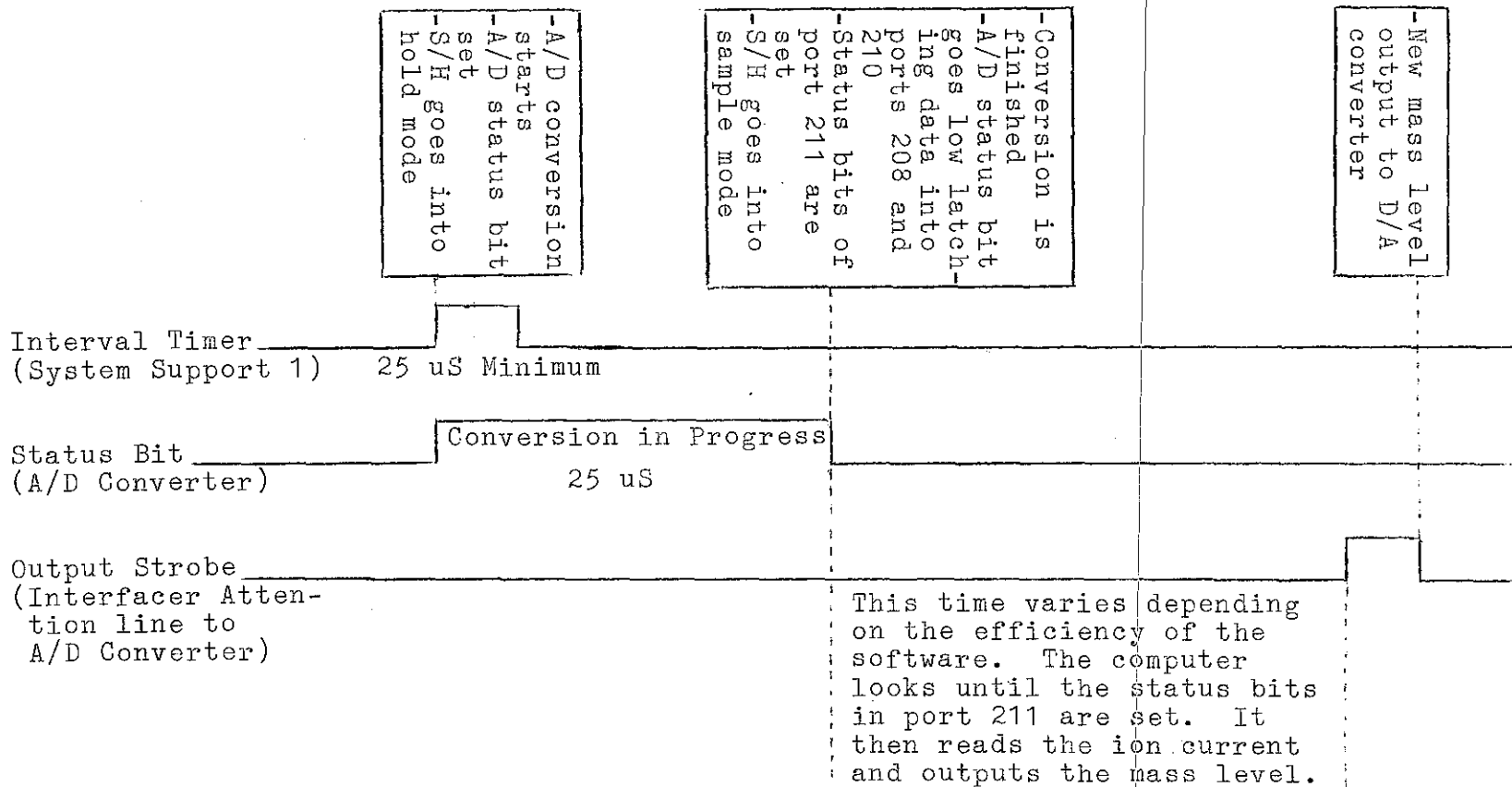


Figure A.4

Timing Diagram for Mass  
Spectrometer/Microprocessor  
Interface





## APPENDIX B

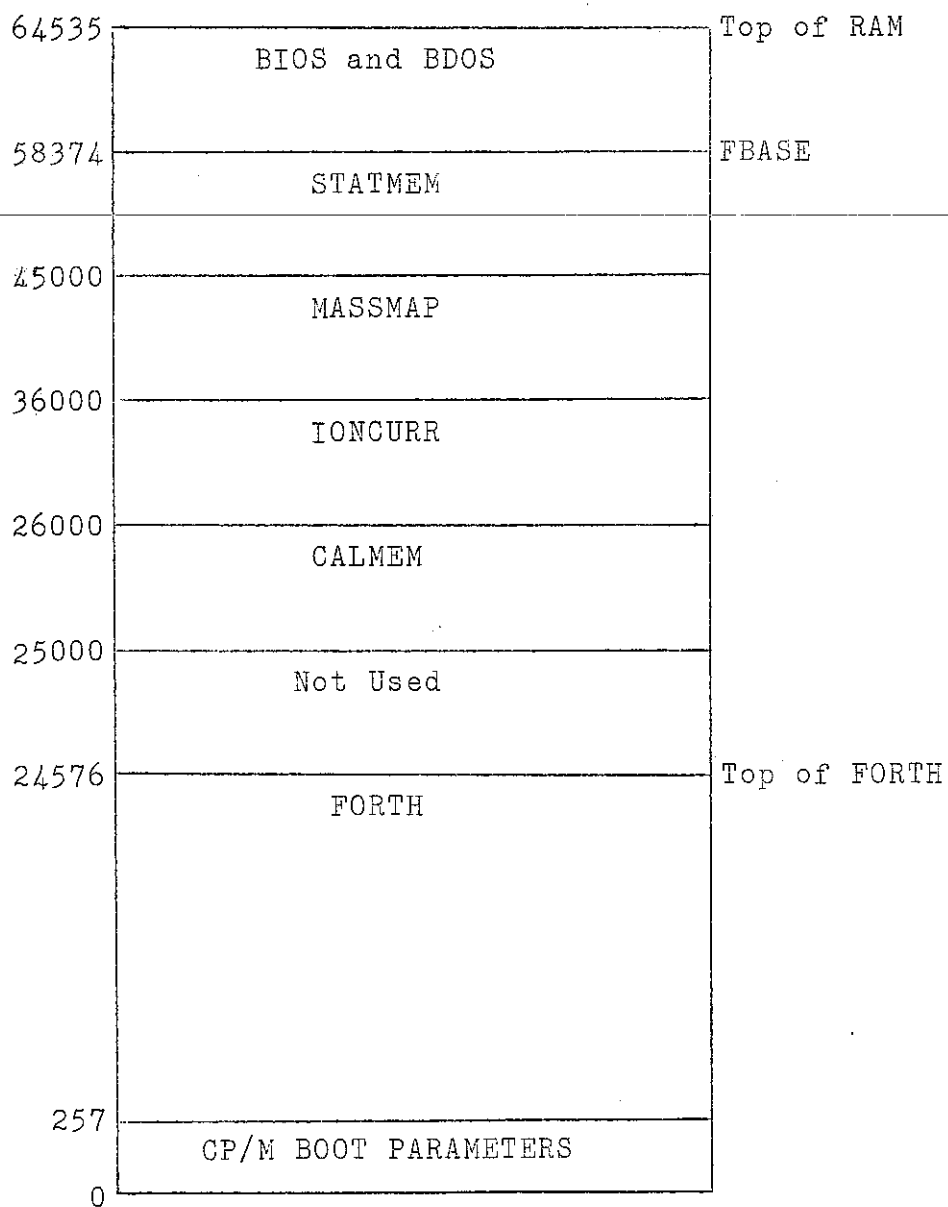
### MASS SPECTROMETER/MICROPROCESSOR INTERFACE SOFTWARE

The following discussion assumes a working knowledge of CP/M and fig-FORTH with BDOS VIRTUAL. The goal of the programming was to provide a system in which the computer would interact with the user for the purposes of calibration, control, data collection and data reduction. In the examples, information which has been entered by the operator as a result of a computer directive or question will be underlined. Only those words implemented by the user for doing a job will be discussed. For the definitions of more basic words, used in constructing the words discussed here, see the glossary in Appendix C. For the actual FORTH programs used to implement the interface, see the listing of FORTH screens in Appendix E.

#### B.1 Memory Map and Port Assignments

A memory map is provided in Figure B.1.1 for reference. The low end of memory from 0 to 256 contains the cold boot parameters for CP/M. The transient program area runs from 256 to 58374 where CP/M FBASE begins. When FORTH is assembled from its assembly language source file, it is normally configured for the maximum available RAM. This would mean that the FORTH transient program would fill memory up to FBASE which is location 58374 in our system. Memory

Figure B.1.1

Memory Map for  
Interface Software

space would then be allotted within the FORTH dictionary for buffers and arrays. However, in this system FORTH was configured in such a way that the top of FORTH is 24576. The higher memory is available to FORTH by using the word CONSTANT to define the beginning of locations MASSMAP, IONCURR, CALMEM and STATMEM.

The Z-80 microprocessor chip uses ports for input and output with the outside world. A list of port assignments is provided in Table B.1.1.

## B.2 Calibration

The word CAL is used to calibrate the mass spectrometer. When CAL is typed at the terminal, the computer responds as follows:

```
Enter the run name CALIBRAT000
Number of mass levels? n
Enter mass levels in ascending order
Mass 001      
Mass 002      
      :
Mass  n       Space when ready      OK
```

The run name must be exactly eleven characters long since it will be the CP/M file name under which the calibration parameters will be stored on disk. An example of a code name is shown above. It differs from a standard CP/M name in that it must be exactly eleven characters long and should not contain a period separating file name and file type. After asking for the number of mass levels, *n*, the computer collects the mass levels with the assumption that they are given in ascending order, and sets up an array at CALMEM as

Table B.1.1

Port Assignments for  
Interface Software

Port	Description
52	Initialization and load port for interval <del>timer on Compu-Pro System Support 1 board</del>
208	High byte port for 16 bit D/A converter and 12 bit A/D converter
209	Parallel port for Epson MX-80 printer
210	Low byte port for 16 bit D/A converter and 12 bit A/D converter
211	Status port for Compu-Pro Interfacer II board

shown in Table B.2.1.

The zeros entered are eventually replaced with D/A equivalents to be determined later in the program. A D/A equivalent is defined as a number which, when loaded into the 16 bit D/A converter, will set the mass spectrometer to the center of the mass level to which the D/A equivalent corresponds. Default values of 434 and 45857 are entered for masses 2 and 311 respectively. These are not available for calibration since they are fixed for interpolation purposes.

It was found that each mass,  $x$ , begins at approximately  $(x-2)*147 + 300$ , and returns to baseline at approximately  $(x-2)*147 + 447$ . Therefore, the computer goes to the beginning of each mass entered and steps through the mass range one least significant bit (LSB) at a time, setting the mass level with SETMASS. It also collects an ion current with GETION and adds each value to a unique four byte cell in IONCURR. Note that since IONCURR has 9800 bytes available, and since it may overlap with the memory reserved for MASSMAP and STATMEM, a maximum of 57 mass levels may be entered for calibration. The computer scans through the mass levels twenty times, adding the results of each scan to the contents in memory. CAL then uses NORM to divide each double precision number in location  $\text{IONCURR} + 4n$  by twenty leaving the single precision number in location  $\text{IONCURR} + 2n$ .

The mass spectrometer experiences occasional spikes which cause problems when determining the location of the

Table B.2.1

Initial Calibration Array  
at CALMEM

Memory Location (Offset from CALMEM)	Memory Contents
0	n
2	2
4	434
6	Mass 1
8	0
10	Mass 2
12	0
⋮	⋮
$4n + 2$	Mass n
$4n + 4$	0
$4n + 6$	311
$4n + 8$	45857

maximum intensity for a given mass level. A number of different approaches were tried and the one selected was found to be simple, yet affective. For each mass level with its corresponding series of 147 numbers, the computer does the following test for each set of three consecutive numbers (x, y and z):

```

      IFF    y-x >  z-x
      THEN   y = (x+z)/2

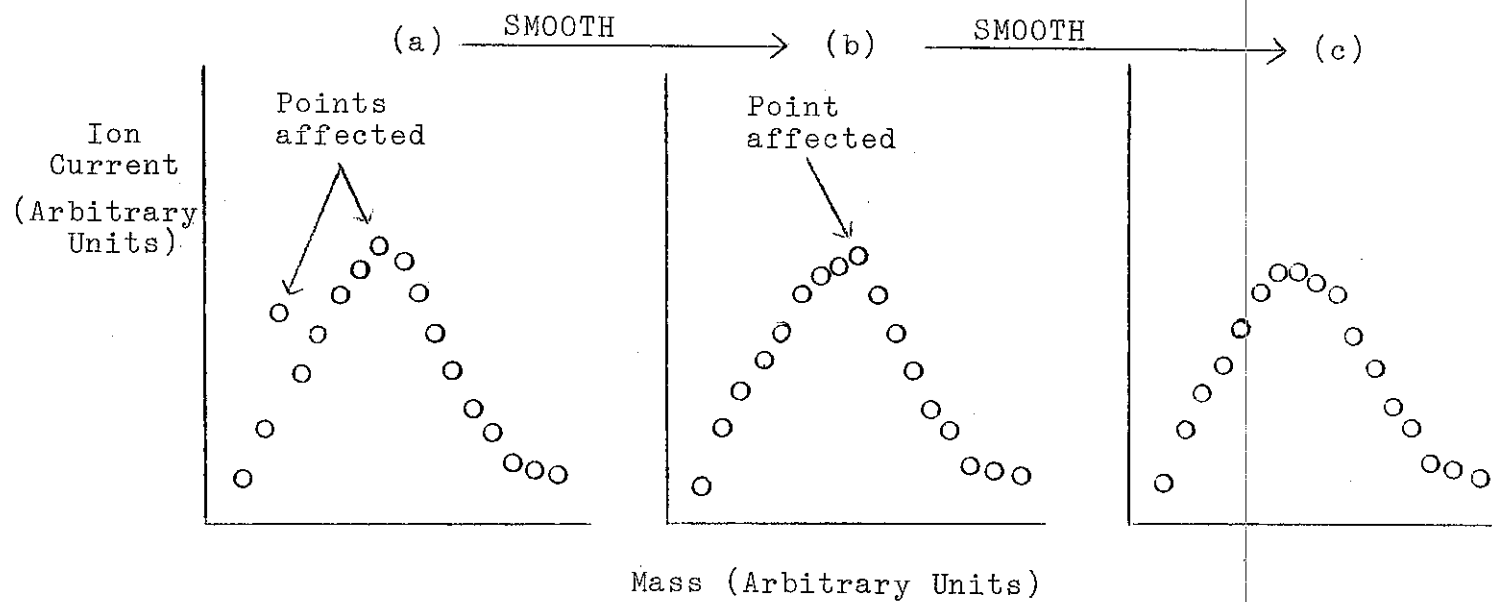
```

This serves to remove spurious signals. The program for this is called SMOOTH. For example, SMOOTH applied twice on the points in (a) would produce the points in (c) as shown in Figure B.2.1. As seen in (b), it also changes the peak. However, applying SMOOTH twice tends to remedy this situation. The error involved for 147 points for each mass level is not considered significant.

The next step is to determine where the maximum ion current is obtained for each mass level and to store its D/A equivalent, with its corresponding mass, in CALMEM. MAXIMUM does this by finding the largest sum of seven consecutive numbers for each set of 147 ion currents corresponding to a given mass level. The D/A equivalent corresponding to the middle ion current's location is then stored with its mass level in CALMEM. Simply finding the maximum ion current might give erroneous results since there is noise in the background which can cause a point to be slightly high even though it does not correspond to the maximum of the mass level. Taking a summation of seven consecutive points tends to average this noise out. The

Figure B.2.1

Effect of SMOOTH on a Typical  
Set of Data Points in IONCURR





number of seven was chosen because of software limitations which prevent the convenient inclusion of more points.

Finally, CALMEM is stored on disk under the CP/M file name entered earlier. For flexibility, MASSARRAY was not incorporated into CAL. It may be necessary to calibrate the spectrometer for different applications (which differ in the resolution setting, emission current, damper setting, etc.) on the same day. The different calibrations can be stored under separate CP/M file names and implemented by typing MASSARRAY at the terminal. The computer will respond with:

Enter the run name CALIBRAT000

Typing in the appropriate CP/M file name and hitting return causes the computer to read the file into CALMEM. It then does an interpolation on the values found there to determine D/A equivalents for masses 2 to 311. These D/A equivalents are stored in consecutive locations in MASSMAP beginning with 2 amu at MASSMAP + 4. Mass x is found at MASSMAP + 2\*x.

This is sufficient for the applications described here. However, room has been reserved in memory to provide for dividing MASSMAP's contents an arbitrary number of times to provide for high resolution scanning capability. The contents of MASSMAP are used to set a mass by simply fetching the appropriate memory contents onto the stack and using SETMASS to load the D/A converter.

### B.3 Control and Data Collection

When JSCAN is typed at the terminal, the computer responds as follows:

```

Enter the run name _____
Samples per mass level?  ____
Number of scans?  ____
Sample rate?  ____
Number of mass levels?  ____
Enter masses in ascending order
Mass 001  ____
Mass 002  ____
:
Mass  n  ____ Space when ready  ____
Another run(0 if no)?  X
Another run(0 if no)?  X
:
Another run(0 if no)?  0 OK

```

Once again, the run name is a CP/M file name, differing from standard CP/M as described earlier, whose type should be a three digit number. The number of scans determines how many times the computer will go through the masses selected. The samples per mass level determines how many times the ion current will be read for a given mass during a given scan. The parameters and data are stored in IONCURR as shown in Figure B.3.1. The data is stored unmodified in such a way that data reduction routines can locate any scan and any sample. For this reason, the parameters must also be stored on disk with the data.

Some special considerations must be given to selecting the sample rate. The word INTTIME uses the number entered under JSCAN to calculate a number suitable for the interval timer. When TIMESSET initializes the interval timer for pulse mode and loads the timer with the number deter-

Figure B.3.1

Memory Organization for Parameters  
and Data Gathered During a Set  
Under JSCAN  
(Offset from IONCURR)

0	Number of masses (n)
2	Not used
4	Number of scans (y)
6	Sample rate
8	Samples per mass level
10	Number of cells of data
	Not used
20	Mass 1
22	D/A equivalent for mass 1
	⋮
16 + 4n	Mass n
18 + 4n	D/A equivalent for mass n
	⋮
200	Samples for first mass and first scan
200 + 1*x*2	Samples for second mass and first scan
	Samples for nth mass and first scan
	⋮
200 + n*x*2	End of first scan
	Intermediate scans
200 + n*x*y*2	End of yth scan

mined by INTTIME, the timer will pulse the required number of times per second signaling the 12 bit A/D converter to do a conversion at each pulse. In JSCAN, the slowest rate for which the timer can be set is 31 samples per second. To go slower it would be necessary only to gather the ion current every other time or every third time the timer pulses. By varying the interval timer, it was found that the quadrupole needs a minimum of 0.010 seconds to jump 1 amu, 0.012 seconds to jump 10 amu and 0.013 seconds to jump 16 amu. This corresponds to sample rates of 100, 85 and 80 samples per second respectively. For safety, it is best to stay between 31 and 60 samples per second. The maximum rate at which the computer can gather samples when sitting on the same mass level is 400 samples per second.

When the computer has completed the required number of scans, it will store the contents of IONCURR on disk drive 2 under the CP/M file name entered. The file type is then incremented with INCASCII and the computer asks if another run is desired. Typing anything except a zero causes the computer to repeat the above sequence according to the parameters originally entered. The new contents of IONCURR are stored on disk under the new file name (with the incremented file type). This way a set of runs may be created which have the same file name and sequential file types. The process may be repeated as often as desired until a zero is entered ending the program.

#### B.4 Data Reduction

Data can be retrieved from disk with READSCAN. The data is placed in IONCURR in the format shown in Figure B.3.1. MOVION will cause the data beginning at IONCURR + 200 to be moved to STATMEM. This allows the data to be altered without losing the original.

JSTAT and JSTAT1 were written to handle data collected by JSCAN. Typing JSTAT at the terminal causes the computer to respond as follows:

```
Enter the run name ____  
Number of sets? ____
```

JSTAT collects the sets one set at a time with READSCAN. It then removes the spurious signals with KICKSORT. The average and average deviation for all the samples for a given scan, set and mass level are determined and output to the terminal. The average and average deviation of all the scans for a given set and mass level is determined and output to the terminal. If more than one set is desired, the program will increment the file type and perform the operations described above on the next set. It will do this for the required number of sets. JSTAT1 was written for the special case in which only one scan is taken.

#### B.5 Use of Software

Figure B.5.1 is an example of a complete session with the mass spectrometer/microprocessor system including use of the words discussed above. It was obtained through use of the echo print function of CP/M.

Figure B.5.1

Example of a Complete Session with the  
Mass Spectrometer/Microprocessor System

Screen	Comments
CAL Enter the run name; <u>CALIBRAT000</u>	
Number of mass levels? <u>3</u>	Mass levels 18, 28 and
Enter masses in ascending order	44 chosen for calibration
Mass 001 <u>18</u>	
Mass 002 <u>28</u>	
Mass 003 <u>44</u> Space when ready <u>OK</u>	
MASSARRAY Enter the run name; <u>CALIBRAT000</u>	
OK	
JSCAN Enter the run name; <u>JUMPSCAN000</u>	
Samples per mass level? <u>50</u>	
Number of scans? <u>2</u>	
Sample rate(in samples/sec)? <u>40</u>	
Number of mass levels? <u>2</u>	
Enter masses in ascending order	
Mass 001 <u>18</u>	
Mass 002 <u>28</u> Space when ready <u>  </u>	Mass levels 18 and 28
Another run(0 if no)? <u>A</u>	chosen for mass analysis
Another run(0 if no)? <u>00K</u>	
JSTAT	
Enter the run name; <u>JUMPSCAN000</u>	
Number of sets? <u>2</u>	
SET 001	
818	67
2856	18
881	68
2874	18
ALL SCANS	Average and average deviation for masses 18 and 28 for the first set and first scan
018	68
028	17
	Average values for above scans in set 001 with the mass levels indicated. The average deviation is also shown
SET 002	
951	96
2888	18
904	63
2890	17
ALL SCANS	Same as the above, except for set 002
018	68
028	17

## APPENDIX C

### GLOSSARY OF FORTH WORDS USED TO IMPLEMENT THE MASS SPECTROMETER/MICROPROCESSOR SYSTEM

+2! Used in the form; d1 addr ---

Causes the double precision number d1 to be added to the cell contents at addr.

10\*\* Used in the form; n1 --> n2(10\*\*n1)

Raises 10 to the n1 power and leaves the result on the stack.

AVERAGE Used in the form; n1 addr ---

Determines the average and average deviation of n1 numbers beginning at addr. The intermediate sum is a double precision number. The average and average deviation are stored at AV and AD respectively.

AVOUT Used in the form; ---

Outputs the contents of AV and AD to the terminal. The leftmost digit of the contents of AD is always 14 spaces to the right of the leftmost digit of the contents of AV.

CAL Used in the form; ---

A complete discussion of CAL is given in Appendix B.

1CAL Used in the form; ---

This is the part of CAL which reads the CP/M file name and sets up the initial array in CALMEM as shown in Table B.2.1.

2CAL Used in the form; ---

This is the part of CAL which scans the mass levels chosen in 1CAL in 147 one bit increments and adds the results of each scan to 32 bit locations in IONCURR.

CLRION Used in the form; n1 ---

Clears 10,000 bytes of memory beginning at IONCURR.

CR'S Used in the form; n1 ---

Causes n1 carriage returns at the terminal.

GETION Used in the form; --> n1

Collects a 12 bit value from the A/D converter and leaves it on the stack. It also clears the status bit in port 211. The twelve bit value is treated like a 16 bit value.

HEADING Used in the form; ---

Prints a four column heading at the terminal indicating set, mass average and average deviation. Used with STAT routines.

HEADING2 Used in the form; ---

Prints a three column heading at the terminal indicating set, average and average deviation. Used with STAT routines when only one mass is being monitored.

HILODROP Used in the form; n1 addr ---

Looks at n1 single precision numbers beginning at addr and replaces the high and low values with zeros. The memory is adjusted to place the zeros at the end of the series of numbers.

INCASCII Used in the form; addr ---

Causes the number stored in three consecutive bytes in ASCII format, beginning at addr, to be incremented. It is used to increment the CP/M file type for storage or retrieval of successive sets of data on disk.

1INIT Used in the form; ---

Causes the message "Number of scans?" to be printed at the terminal. The computer then waits for a five digit number or a carriage return, whichever comes first, and stores the number at NUMSCAN. Determines the number of scans in SCAN routines.

2INIT Used in the form; ---

Causes the message "Number of sets?" to be printed at the terminal. The computer then waits for a five digit number or a carriage return, whichever comes first, and stores the number at NUMSET. Determines the number of sets to be processed in STAT routines.

3INIT Used in the form; ---

First causes the computer to print the message "Starting mass?" and then waits for a five digit number or a carriage return, whichever comes first. The number is stored at 1MASS. The computer then does a carriage return and prints the message "Final mass?". It waits for another five digit number or carriage return and stores this number at 2MASS. Can be used for continuous scans.



4INIT Used in the form; ---

Causes the message "Sample rate(in samples/sec)?" to be printed at the terminal. The computer then waits for a five digit number or a carriage return, whichever comes first, and stores this number at RATESAMP. Used by INTTIME to determine a number for the interval timer.

5INIT Used in the form; ---

Causes the message "Samples per mass level?" to be printed at the terminal. The computer then waits for a five digit number or a carriage return, whichever comes first, and stores the number at SAMPLEV. This determines how many samples are taken for a given mass level during a scan.

6INIT Used in the form; ---

Causes the message "Enter the run name;" to be printed at the terminal. The computer then waits for eleven characters and a carriage return and stores these characters, in ASCII format, in eleven consecutive bytes beginning at DATANAM. Used as a CP/M file name and type when storing or retrieving data with SAVEIT or READIT. Unlike CP/M, the name and type must total exactly eleven characters and no period is placed between the name and type. If the type is to be incremented with INCASCII, it must be a three digit number.

7INIT Used in the form; ---

Causes the message "Number of mass levels?" to be printed at the terminal. The computer then waits for a five digit number or a carriage return, whichever comes first, and stores this number at 1MASS. Determines the number of masses sampled by CAL or JSCAN.

8INIT Used in the form; ---

Causes the message "Enter the masses in ascending order" to be printed at the terminal. Marks the point at which masses may be entered under CAL or JSCAN.

INTTIME Used in the form; ---

Uses the value stored at RATESAMP, entered under 4INIT, to calculate a number suitable for the interval timer and stores this number at LOADINT.

JSCAN Used in the form; ---

A complete discussion of JSCAN is given in Appendix B.

JSTAT Used in the form; ---

JSTAT is discussed completely in Appendix B.

JUMPINIT Used in the form; ---

The part of JSCAN which gathers the parameters necessary to do a set and store the results on disk.

JUMPSCAN Used in the form; ---

The part of JSCAN which does the scans, collecting the results in IONCURR, and stores the data and parameters on disk. It is set up to do as many sets as the user wishes and will increment the file type for each set for unique disk storage.

KICKSORT Used in the form; n1 addr ---

If x is one of n1 number beginning at addr and if AV is the average of the other numbers while AD is the average deviation of all the numbers, the following will be done for each number, x:

IFF  $x - AV \geq 2 * AD$  then x is replaced with AV.  
Otherwise, there is no effect.

MASSARRAY Used in the form; ---

MASSARRAY is discussed in Appendix B.

MAXIMUM Used in the form; ---

Finds the largest sum of seven consecutive numbers for a group of 147 numbers in IONCURR which correspond to a given mass level. Takes the location of the middle number of this sum to calculate a D/A equivalent which corresponds to the maximum of the peak. Stores this number at CALMEM in the format discussed in Appendix B.

2MOVE Used in the form; n1 addr1 addr2 ---

Causes n1 cells starting at addr1 to be moved to addr2.

MOVION Used in the form; ---

Causes the data beginning at IONCURR + 200 to be moved to STATMEM. Uses the value stored at IONCURR + 10 to determine the number of values to be moved. Used by STAT routines.

NORM Used in the form; ---

Uses a number stored at IONCURR + 10 to determine how many consecutive double precision numbers, beginning at IONCURR + 200, to divide by 20 leaving the single precision number. Used in CAL to obtain the average value of 20 scans.

PARSAVE Used in the form; ---

Used to save the parameters stored in the first 10 bytes of IONCURR.

READE Used in the form; --> n1

READE causes the computer to wait for five digits or a carriage return, whichever comes first, and places the single precision number on the stack. It uses EXPECT to collect the digits in ASCII format and converts the intermediate ASCII string to a decimal number. The number must not exceed 65535 and commas are not permitted. This allows decimal numbers to be entered as part of a computer directive or question in a program.

READIT Used in the form; addr n1 n2 ---

Causes n1 bytes, starting at addr, to be read from a CP/M file on drive n2 to memory. The CP/M file name is stored in eleven consecutive bytes at DATANAM.

READSCAN Used in the form; ---

READSCAN uses READIT to read a file stored on disk, in the format shown in Figure B.3.1, into IONCURR. It does a preliminary read to obtain the number stored at IONCURR + 10. This number is used to calculate the total number of bytes which is stored in the CP/M file. The name of the file is stored in eleven consecutive bytes at DATANAM.

SAVEIT Used in the form; addr n1 n2 ---

Causes n1 bytes starting at addr to be saved in a CP/M file on drive n2. The file name is stored in eleven consecutive bytes starting at DATANAM.

SET Used in the form; n1 ---

Will cause the D/A converter to be set to a value stored at MASSMAP + 2\*n1.

SETMASS Used in the form; n1 ---

Causes the D/A converter to be loaded with the value n1.

SMOOTH Used in the form; ---

See Appendix B for a complete discussion of SMOOTH.

STAT1 Used in the form; --> n1

Uses READSCAN to read a file to IONCURR and moves the data beginning at IONCURR + 200 to STATMEM with MOVION. Leaves the samples per mass level on the stack. Used by JSTAT and JSTAT1.

STAT2 Used in the form; ---

Determines the average and average deviation of sets of data beginning at IONCURR in a manner discussed in Appendix B.

STAT3 Used in the form; ---

Used by JSTAT and JSTAT1 to determine the average and average deviation for all the scans and all the samples taken in a given set for a given mass level. Outputs these values to the terminal. See Appendix B.

2SUM Used in the form; n1 addr --> d2-sum

Adds n1 single precision numbers beginning at addr and leaves the double precision sum.

TERMTEST Used in the form; ---

Causes the computer to wait for a keystroke from the terminal and stores the ASCII character at TERMSTORE. Useful for providing a way out of a program which is user dependent. The program will not continue until a keystroke is entered, and a decision can then be based upon the value of the keystroke.

TESTPORT Used in the form; ---

Halts computer execution until the 12 bit A/D converter signals that a conversion is complete. It does this by continually testing port 211 until the status bit is set.

TIMESSET Used in the form; ---

Initializes the interval timer for pulse mode and loads it with the 16 bit value stored at LOADINT. Usually used in conjunction with INTTIME.

WRITE Used in the form; n1 ---

Causes the number n1 to be output to the terminal as a three digit number while a program is running. The number must be between 0 and 999.

## APPENDIX D

### GLOSSARY FOR VIRTUAL FORTH

Fig-FORTH with BDOS virtual is a modification of fig-FORTH prepared by John Cassady of Oakland in accordance with the "fig" model. The following introduction and glossary was written by Michael Stolowitz and is a publication of the Forth Interest Group. All publications of the Forth Interest Group are public domain. They may be further distributed by inclusion of this notice:

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P.O. Box 1105  
San Carlos, CA 94070

BDOS VIRTUAL is a modification to the FORTH word R/W which causes FORTH to access disk blocks from CP/M files using BDOS calls rather than directly accessing the disk through CP/M BIOS calls. While this does result in a speed reduction for the FORTH system, the convenience of using the system for CP/M users, the ability to communicate with other CP/M compatible software and the resulting portability of the resulting FORTH system to a wide range of hardware environments makes the modification attractive.

`%DEFLT     n1 --- p1`

Open the default file FORTH.BLK on the current drive. An FCB is created and the file is opened and linked. A pointer to the FCB p1 is returned while n1 is discarded. See `%OPEN` and `%LINK`.

`%LINK     p1 --- p1`

Link the FCB of the open file pointed to by p1 in the list of open files pointed to by the user variable FILES.

`%MAKE     n1 --- p1`

Used in the form:     `%MAKE   cccc   dddd`

~~Will create an FCB for the file named dddd (in UFN~~  
format) on the drive specified by n1. (n1 = 1 for drive A:    n1 = 2 for drive B:    ...    n1 = 0 for the current drive). A pointer to the FCB, p1, is returned for subsequent opening and linking. The word cccc (the file ID) will be defined and when executed will return p1.

`%OPEN     n1 n2 --- n3`

Open the file whose FCB is pointed to by p1 and determine its size. If the file cannot be opened, an error message is given.

`BDOS     n1 n2 --- n3`

Call the CP/M BDOS function n2 with parameter n1. Return the result n3. BDOS is called via a jump instruction at memory address 5. The function n2 is placed in the BC register pair and the entry parameter n1 is placed in the DE register pair. The result n3 is taken from the accumulator.

`BDOS     n1 n2 ---`

Call the CP/M BDOS using BDOS. The result is stored in the variable DISK-ERROR.

`CHR     --- n    If executing  
         ---     If compiling`

Used in the form:     `CHR c`

Used while executing will place the ASCII value of the character c on the stack. If compiling, a literal of value n will be compiled. The effect of CHR is identical to using numeric literals. Used for improved readability.

`CLOSE     p1 ---`

Will cause the user variable FILES to be linked to the file opened prior to the one whose FCB is pointed to by p1. The file pointed to by p1 and all files opened after it are removed from the virtual memory. No CP/M calls are made.

GO ---

Used in the form: GO nnnn

The dictionary word nnnn will be executed repeatedly until a key is pressed on the terminal.

OPEN n1 ---

Used in the form: OPEN cccc dddd

Will create an FCB for the file dddd on the drive specified by n1. The file will be opened and linked. The word cccc will be defined. When executed, cccc will return a pointer to the files FCB. See %OPEN and %LINK.

R/W addr blk flg ---

The block of virtual memory specified by blk is read or written to memory location addr. If flg is true, the block is read. If it is false, the block is written. If no files are opened, R/W will open the default file by calling %DEFLT. If the requested block is outside of the virtual range provided by all of the open files, the message OUT OF VIRTUAL RANGE will be given. Disk read or write errors result in the message DISK ERROR.

SYSGEN ---

Used in the form: SYSGEN  
Save nn  
BYE  
A SAVE nn VFOR.COM

The cold boot parameters are adjusted so that execution of COLD will retain all of the words in the dictionary at the time of the SYSGEN. It will also calculate and display the number of blocks which must be "SAVED" under CP/M to store an executable image of the system. BYE and a CP/M SAVE of the specified number of blocks must immediately follow the SYSGEN.

UFN addr ---

A CP/M unambiguous file name is accepted from the input stream and stored at location addr. The UFN consists of a file name of up to eight characters followed by a file type of up to three characters. If both name and type are present, they must be separated by a period. The name is stored left justified and blank filled in the first eight characters at addr. The type is stored also left justified and blank filled in the next three locations.

## APPENDIX E

### FORTH SCREENS LOADED TO IMPLEMENT THE MASS SPECTROMETER/MICROPROCESSOR INTERFACE

The following pages contain the actual FORTH screens which were loaded to implement a microprocessor controlled mass spectrometer system. Loading screen 96, with the FORTH word LOAD, causes all of the system screens to be loaded. Screens 95 and 96 also serve as a directory. Words not usually found in standard fig-FORTH are defined at the bottom of the screens in which they appear. For a discussion of some of these words, and an alphabetical listing with their definitions, see Appendixes B and C respectively.

Loading the screens each time the system is brought up is time consuming. Therefore, SYSGEN (see Appendix D) was used to make them a permanent part of the FORTH system.

The screen copies were obtained on the Epson MX-80 printer through use of the CP/M echo print utility and the FORTH words LIST and TRIAD.



SCR # 51

```

0 ( UTILITIES )
1
2 : 2SWAP ROT >R ROT R> ;
3
4 : PICK DUP + SP@ + @ ; ( N --- Copy Nth item to top )
5
6 : 2DROP DROP DROP ;
7
8 : 2MOVE 3 PICK 0 DO 2 PICK 1 4 * + 2@
9   3 PICK 1 4 * + 2! LOOP 2DROP DROP ;
10
11 ;S
12
13 ( 2MOVE used in the form;  n1 addr1 addr2 ---
14   Will cause n1 cells starting at addr1 to be moved
15   to addr2. )

```

106

SCR # 52

```

0 ( UTILITIES CONT. )
1
2 : +2! DUP 2SWAP ROT 2@ D+ ROT 2! ;
3
4 : D- DMINUS D+ ;
5
6 : MOVE 3 PICK 0 DO 2 PICK 1 2 * + @
7   2 PICK 1 2 * + ! LOOP 2DROP DROP ;
8 ;S
9
10 ( +2! used in the form;  d1 addr ---
11   Will cause the double precision number d1 to be added
12   to the cell contents at addr. )
13
14
15

```

SCR # 53

```

0 ( UTILITIES CONT. )
1
2 : CR'S 0 DO CR LOOP ;
3
4 : WRITE 2 0 DO 10 /MOD LOOP 3 0 DO 48 + EXIT LOOP 32 EXIT ;
5 : 10** DUP 1 > IF 10 SWAP 1 DO 10 * LOOP ELSE
6   0= IF 1 ELSE 10 ENDIF ENDIF ;
7 ;S
8 ( CR'S used in the form;  n1 ---
9   Will cause n1 carriage returns at the terminal.
10
11   WRITE used in the form;  n1 ---
12   Will cause the number n1 to be output to the terminal
13   under software control.
14   10** used in the form;  n1 --> 10**n1
15   Raises 10 to the n1 power. )

```

SCR # 54

```
0 ( READE-For numeric input from terminal          JDW 8/81 )
1
2 0 VARIABLE DIGITS 0 VARIABLE TENS
3 0 VARIABLE VALUE 0 VARIABLE Terval 5 ALLOT
4
5 : CONVERT BEGIN DUP 0= WHILE DIGITS @ 1+ DIGITS ! DROP
6 REPEAT 1 TENS ! 5 DIGITS @ - 0 DO 48 - TENS @ ! VALUE
7 @ + VALUE ! TENS @ 10 * TENS ! LOOP VALUE @ ;
8
9 : READE Terval 5 0 FILL 0 DIGITS ! 0 VALUE ! Terval 5
10 EXPECT 5 0 DO Terval 1 + C@ LOOP CONVERT ;
11 ;S
12 ( READE used in the form;  --> n1
13 When READE appears, the computer will wait for five digits
14 or a return and place the single precision number on the
15 stack. The number must not exceed 65535. No commas. )
```

107

SCR # 55

```
0 ( 2SUM          JDW 1/82 )
1
2
3
4 : 2SUM SWAP 0. ROT 0 DO 3 PICK
5 I 2 * + @ 0 D+ LOOP ROT DROP ;
6
7
8
9 ;S
10 ( 2SUM used in the form;  n1 addr --> d1-sum
11 Adds n1 single precision numbers starting at addr and
12 leaves the double precision sum. )
13
14
15
```

SCR # 56

```
0 ( READIT          JDW 9/81 )
1
2 0 VARIABLE DATANAM 12 ALLOT 0 VARIABLE FCB 36 ALLOT
3
4 : UDN DATANAM SWAP 11 CMOVE ;
5
6 : READIT ( ADDR N DRV --- )
7 FCB DUP 36 0 FILL DUP 1+ UDN C!          ( SETUP FCB )
8 FCB 15 BDOS DISK-ERROR @ 255 = 9 ?ERROR  ( OPEN THE FILE )
9 OVER + SWAP DO
10 I 26 BDOS FCB 20 BDOS DISK-ERROR @ 12 ?ERROR
11 128 +LOOP FCB 16 BDOS DISK-ERROR @ 255 = 13 ?ERROR ;
12 ;S
13 ( READIT used in the form;  addr n1 n2 ---
14 Will cause n1 bytes to be read from a CP/M file on drive
15 n2, whose name is at DATANAM, to address addr. )
```

SCR # 57

```

0 ( SAVEIT                                JDW 9/81 )
1
2 : SAVEIT ( ADDR N DRV --- )
3 FCB DUP 36 0 FILL DUP 1+ UDN C!          ( SETUP FCB )
4 FCB 19 BDOS                               ( DELETE OLD FILES )
5 FCB 22 BDOS DISK-ERROR @ 255 = 11 ?ERROR ( MAKE THE FILE )
6 OVER + SWAP DO
7 I 26 BDOS FCB 21 BDOS DISK-ERROR @ 12 ?ERROR
8 128 +LOOP FCB 16 BDOS DISK-ERROR @ 255 = 13 ?ERROR ;
9 ;S
10
11
12
13 ( SAVEIT used in the form;  addr n1 n2 ---
14 Will cause n1 bytes to be saved in a CP/M file on drive
15 n2 from address addr. The file name is at DATANAM.      )

```

108

SCR # 58

```

0 ( AVERAGE                                JDW 1/82 )
1
2 0 VARIABLE AV 0 VARIABLE AD
3
4 : AVERAGE 2DUP 2SUM                      ( TAKE SUM OF DATA POINTS )
5 4 PICK M/ SWAP DROP AV !                 ( FIND AVERAGE - STORE AT AV )
6 0 3 PICK 0 DO                            ( TAKE SUM OF DEVIATIONS )
7 2 PICK I 2 * + @
8 AV @ - ABS + LOOP
9 3 PICK / AD ! 2DROP ; ( FIND AVERAGE DEVIATION - STORE AT AD )
10 ;S
11 ( AVERAGE used in the form;  n1 addr ---
12 Determines the average and average deviation of n1 single
13 precision numbers beginning at addr. The intermediate sum
14 is double precision. Stores the average and average
15 deviation at AV and AD respectively.      )

```

SCR # 59

```

0 ( KICKSORT                                JDW 2/82 )
1
2 : KICKSORT 2DUP 2DUP AVERAGE 2SUM
3 2SWAP 2 PICK 0 DO DUP I 2 * + @
4 AV @ - ABS AD @ 2 * > IF 4 PICK 4 PICK    ( X-AV > 2*AD? )
5 3 PICK I 2 * + @ 0 D- 4 PICK 1 -
6 M/ SWAP DROP 2 PICK I 2 * + !
7 ELSE ENDIF LOOP 2DROP 2DROP ;
8 ;S
9 ( KICKSORT used in the form;  n1 addr ---
10 If X is one of n1 numbers beginning at addr and AV is the
11 average of the other numbers while AD is the average deviation
12 of all the numbers, the following test will be done for
13 each number X;
14 If X-AV > 2*AD, X is replaced with AV.
15 Otherwise, no effect.                      )

```

SCR # 60

JDW 2/82 )

109

```
0 ( HILODROP
1 0 VARIABLE HI 4 ALLOT 0 VARIABLE LO 4 ALLOT
2 : HILODROP 0 3 PICK 0 DO
3   2 PICK I 2 * + 0 /
4   0= IF DUP I 2 * + DUP
5   HI ! 0 ELSE HI 0 0 ENDIF
6   LOOP DROP
7   5000 3 PICK 0 DO 2 PICK I 2 * +
8   0 / 0= IF LO 0 0
9   ELSE DUP I 2 * +
10  DUP LO ! 0
11  ENDIF LOOP DROP
12  0 DUP HI 0 ! LO 0 !
13  2 0 DO 2 PICK 1 - 0 DO   ( MOVE 0's TO LAST MEMORY POSITIONS )
14  -->
15
```

SCR # 61

```
0 ( HILODROP CONT.
1
2   DUP I 2 * + 0 0= IF
3   DUP I 2 * + DUP DUP 2+ 0 SWAP !
4   2+ 0 SWAP ! ELSE ENDIF LOOP LOOP 2DROP ;
5 ;S
6 ( HILODROP used in the form;  n1 addr ---
7   Looks at n1 values in single precision format starting
8   at addr and replaces the high and low values with 0's
9   and places these 0's at the high end of memory.
10
11
12
13
14
15
```

SCR # 62

```
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
```

SCR # 69

```

0 ( INITIALIZATION routines for mass spec scans      JDW 9/81 )
1
2 0 VARIABLE NUMSCAN 0 VARIABLE NUMSET 0 VARIABLE SAMPLEV
3 0 VARIABLE 1MASS 0 VARIABLE 2MASS 0 VARIABLE RATESAMP
4
5 : 1INIT ." Number of scans? " READE NUMSCAN ! CR ;
6
7 : 2INIT ." Number of sets? " READE NUMSET ! CR ;
8
9 : 3INIT ." Starting mass? " READE 1MASS ! CR
10 ." Final mass? " READE 2MASS ! CR ;
11
12 : 4INIT ." Sample rate(in samples/sec)? "
13 READE RATESAMP ! CR ;
14
15 -->

```

110

SCR # 70

```

0 ( INITIALIZATION routines continued )
1
2 : 5INIT ." Samples per mass level? " READE SAMPLEV ! CR ;
3
4 : 6INIT ." Enter the run name; " DATANAM 12 EXPECT CR ;
5
6 : 7INIT ." Number of mass levels? " READE 1MASS ! CR ;
7
8 : 8INIT ." Enter masses in ascending order " ;
9 ;S
10 ( 1INIT-7INIT used in the form; --- n1
11 Will cause computer to wait for specified parameters to be
12 entered from terminal. Used to enter parameters from the
13 terminal for mass spectrometer and data reduction routines.
14 8INIT is simply a message to mark point at which mass levels
15 may be entered from the terminal. )

```

SCR # 71

```

0 ( INTIME and TIMESET      JDW 9/81 )
1
2 0 VARIABLE LOADINT
3
4 : INTIME 19670 RATESAMP 0 / 100 *      ( CALCULATE VALUE )
5 LOADINT ! ;      ( STORE AT LOADINT )
6 : TIMESET 52 87 P!      ( INITIALIZE AND LOAD INTERVAL TIMER )
7 LOADINT 1+ C0 LOADINT C0
8 84 P! 84 P! ;
9 ;S
10 ( INTIME uses RATESAMP to calculate a number suitable for
11 the interval timer and stores it at LOADINT. This
12 determines how often a sample is taken.
13
14 TIMESET initializes the interval timer for pulse mode and
15 loads it with the 16 bit value LOADINT. )

```

SCR # 72

```

0 ( INCASCII                                JDW 9/81 )
1
2 : INCASCII 3 0 DO DUP I + C@ 48 - ( CONVERT TO DECIMAL NUMBER )
3   SWAP LOOP SWAP 2SWAP 10 * SWAP
4   100 * + + 1+                               ( INCREMENT )
5   100 /MOD SWAP 10 /MOD 2SWAP                ( CONVERT TO ASCII FORMAT )
6   SWAP 3 0 DO DUP I + ROT 48 +
7   SWAP C! LOOP DROP ;
8 ;S
9
10
11 ( Used in the form;  addr ---
12   Will cause a number stored in ASCII format at addr in
13   three consecutive bytes to be converted to a decimal
14   number, incremented, converted back to a number in
15   ASCII format and stored at addr. )

```

SCR # 73

```

0 ( SETMASS, TESTPORT and GETION            JDW 10/81 )
1
2   26000 CONSTANT IONCURR
3   25000 CONSTANT CALMEM 0 VARIABLE MASSLEV
4
5 : SETMASS MASSLEV ! MASSLEV C@ MASSLEV 1+ C@ 210 P! 208 P! ;
6 : TESTPORT BEGIN 211 P@ 208 > UNTIL ;
7 : GETION 208 P@ 210 P@ 256 * + ;
8 ;S
9
10 ( SETMASS used in the form;  n1 --- Will cause the
11   16 bit D/A converter to be loaded with the value n1.
12   TESTPORT halts execution until the 12 bit A/D converter
13   signals that a conversion is complete.
14   GETION used in the form;  --- n1 Collects a 12 bit
15   value from the A/D converter and leaves it on the stack. )

```

SCR # 74

```

0 ( CLRION and TERMTEST                     JDW 1/81 )
1
2 0 VARIABLE TERMSTORE
3
4 : CLRION IONCURR 10000 0 FILL ;
5
6 : TERMTEST TERMSTORE 1 EXPECT ;
7
8
9 ;S
10
11 ( CLRION clears 10000 memory locations starting at IONCURR.
12
13   TERMTEST halts exeution until a keystroke is entered. )
14
15

```

SCR # 75

```

0 ( 1CAL                                     JDW 1/82 )
1 : 1CAL CALMEM 50 0 FILL                     ( INITIALIZE CALMEM )
2 2 CALMEM 2+ ! 434 CALMEM 4 + !             ( DEFAULT VALUE FOR MASS 2 )
3 6INIT                                       ( NAME FOR CP/M FILE STORE )
4 7INIT 8INIT 1MASS 0
5 DUP DUP 4 * 6 + DUP CALMEM
6 + 311 SWAP ! 2+ CALMEM +
7 45857 SWAP !                               ( DEFAULT VALUE FOR MASS 311 )
8 CALMEM ! 0 DO CR ." Mass "                 ( COLLECT MASS LEVELS )
9 I 1+ WRITE READE
10 CALMEM 6 + 4 I * + ! LOOP ;
11 ;S
12 ( 1CAL reads a file name for eventual disk storage of an array
13 which is set up in the following format where C is # masses;
14 C 2 434 M1 00 M2 00.....MC 00 311 45857
15 0,1 2,3 4,5 6,7 8,9 10,11 12,13 4C+2 4C+4 4C+6 4C+10 )

```

112

SCR # 76

```

0 ( 2CAL                                     JDW 1/82 )
1
2 : 2CAL CLRION                               ( INITIALIZE IONCURR )
3 ." Space when ready "
4 TERMTEST                                   ( WAIT FOR KEYSTROKE )
5 10000 LOADINT ! TIMESSET                   ( SET INTERVAL TIMER )
6 20 0 DO CALMEM 0 0 DO CALMEM 6 +           ( SET MASS LEVEL AND WAIT )
7 4 I * + 0 147 0 DO DUP 2 - 147 *
8 300 + I + SETMASS TESTPORT                 ( SET MASS LEVEL AND WAIT )
9 GETION 0 IONCURR J 588 * +                 ( GET ION CURRENT AND STORE )
10 4 I * + +2!
11 LOOP DROP LOOP LOOP ;
12 ;S
13 ( 2CAL scans the mass levels stored in CALMEM by 1CAL and
14 adds the result of each scan to 32 bit locations in
15 IONCURR in a consecutive manner. )

```

SCR # 77

```

0 ( NORM and SMOOTH                         JDW 1/82 )
1
2 : NORM CALMEM 0 147 * 0 DO IONCURR 4 I * +
3 20 20 M/ SWAP DROP IONCURR 2 I * + ! LOOP ;
4
5 : SMOOTH CALMEM 0 147 * 1 - 1 DO IONCURR
6 I 2 * + DUP 0 SWAP DUP 2 - 0 DUP ROT 2+
7 0 - ABS ROT ROT - ABS SWAP > IF IONCURR
8 I 2 * + DUP 2+ 0 SWAP DUP 2 - 0 ROT + 2 /
9 SWAP ! ELSE ENDIF LOOP ;
10 ;S
11 ( NORM divides each double precision number in IONCURR
12 by 20 and leaves the single precision number.
13 SMOOTH does the following on each series of three numbers
14 (x,y,z) in IONCURR; y=(x+z)/2 IFF ABS(y-x) > ABS(z-x)
15 It serves to remove spurious signals. )

```

SCR # 78

JDW 1/81 )

113

```

0 ( MAXIMUM
1 : MAXIMUM CALMEM @ 0 DO 0 0 140
2 2 DO IONCURR J 294 * + I 2 * +
3 7 0 DO DUP I 2 * + @ SWAP LOOP ( COLLECT 7 CONS. NUMBERS )
4 DROP + + + + + ( ADD " " " " )
5 2DUP < IF ( PERFORM TEST; < LAST SUM? )
6 SWAP DROP SWAP DROP I 4 + SWAP ( IF TRUE, KEEP NEW VALUE )
7 ELSE DROP ENDIF ( IF FALSE, DISCARD NEW VALUE )
8 LOOP DROP CALMEM @ + I 4 * + @ ( COMPUTE MASS LEVEL )
9 2 - 147 * 300 + +
10 CALMEM @ + I 4 * + ! LOOP ( STORE VALUE AT CALMEM )
11 CALMEM 50 1 SAVEIT ; ( STORE ON DISK )
12 ;S
13 ( MAXIMUM finds the largest sum of seven consecutive numbers
14 in IONCURR corresponding to a given mass level and takes the
15 middle to compute a D/A equivalent. Stores this at CALMEM. )

```

SCR # 79

JDW 1/82 )

```

0 ( CAL
1
2 : CAL 1CAL 2CAL NORM SMOOTH SMOOTH MAXIMUM ;
3 ;S
4 ( CAL is a calibration routine for the mass spectrometer.
5 When CAL is typed at the terminal, the computer will respond
6 by asking for the CP/M file name of the calibration run, the
7 number of mass levels to be used in the calibration and
8 the identity of these masses in ascending order. The
9 computer then waits for a keystroke from the terminal. When
10 recieved, it scans the mass levels entered 20 times and
11 adds the results of each scan to locations in IONCURR. The
12 increments are 1 LSB of the D/A converter and require 147
13 jumps for each mass level. The computer then divides each
14 location by 20 and kicks out spurious signals. The maximum
15 value for each mass level is found and stored at CALMEM. )

```

SCR # 80

JDW 1/82 )

```

0 ( MASSARRAY
1 36000 CONSTANT MASSMAP
2 : MASSARRAY 6INIT CALMEM 50 1 READIT
3 CALMEM @ 1+ 0 DO CALMEM I 4 * + DUP ( BEGIN INTERPOLATION )
4 @ + @ 0 ROT 4 + @ 0 D- CALMEM I 4 * +
5 DUP @ + @ SWAP 2+ @ - M/ CALMEM I 4 * +
6 DUP @ + @ SWAP 2+ @ DO 2DUP I CALMEM
7 J 4 * + 2+ @ - DUP ROT * ROT ROT M*
8 CALMEM J 4 * + DUP @ + @ SWAP 2+ @ - M/
9 SWAP DROP + CALMEM J 4 * + 4 + @ + MASSMAP
10 I 2 * + ! LOOP 2DROP LOOP ;
11 ;S
12 ( MASSARRAY does an interpolation on the D/A equivalents
13 stored at CALMEM to determine D/A equivalents for mass
14 levels 2-311. These values are stored at MASSMAP in
15 ascending order. )

```



SCR # 81

```

0 ( SET and PARSARE
1
2 : SET 2 * MASSMAP + @ SETMASS ;
3
4
5 : PARSARE 1MASS @ IONCURR ! 2MASS @ IONCURR 2+ ! NUMSCAN
6 @ IONCURR 4 + ! RATESAMP @ IONCURR 6 + ! SAMPLEV @
7 IONCURR 8 + ! ;
8 ;S
9 ( SET used in the form; n1 ---
10 Will cause the 16 bit D/A converter to be set to mass level
11 n1.
12
13 PARSARE saves parameters entered from keyboard in first 10
14 locations in IONCURR in following order;
15 1MASS, 2MASS, NUMSCAN, RATESAMP and SAMPLEV.

```

JDW 3/82 )

114

SCR # 82

```

0 ( JUMPINIT
1
2
3 : JUMPINIT 6INIT 5INIT 1INIT 4INIT
4 7INIT 8INIT 1MASS @ 0 DO CR ." Mass "
5 I 1+ WRITE READE DUP IONCURR 20 + ( STORE MASS LEVELS AND )
6 I 4 * + ! 2 * MASSMAP + @ ( D/A EQUIVALENT/AT IONCURR )
7 IONCURR 22 + I 4 * + ! LOOP
8 INTTIME TIMESET ; ( SET INTERVAL TIMER )
9 ;S
10 ( JUMPINIT goes through an initialization routine to ready
11 the computer to gather ion current values at specified mass
12 levels. It asks for the CP/M file name under which scans
13 will be stored as well as other parameters necessary for a
14 scan.
15

```

JDW 1/82 )

SCR # 83

```

0 ( JUMPSCAN
1 0 VARIABLE OFFSETM
2 : JUMPSCAN BEGIN NUMSCAN @ 0 DO 1MASS @ SAMPLEV @ *
3 2 * I * 200 + OFFSETM ! GETION DROP 1MASS @ 0 DO
4 SAMPLEV @ 0 DO
5 IONCURR 22 + J 4 * + @ SETMASS TESTPORT GETION IONCURR
6 OFFSETM @ + J SAMPLEV @ * 2 * + I 2 * + ! LOOP LOOP
7 LOOP PARSARE IONCURR 1MASS @ SAMPLEV @ * NUMSCAN @ *
8 2 * 200 + DUP IONCURR 10 + !
9 2 SAVEIT DATANAM 8 + INCASCII CR
10 ." Another run(0 if no)? " TERMTST TERMSTORE @
11 48 - 0= UNTIL ;
12 ;S
13 ( JUMPSCAN takes samples from the peaks of mass levels
14 entered under JUMPINIT according the the parameters
15 entered under JUMPINIT.

```

JDW 2/82 )

```

0 ( JSCAN
1 : JSCAN JUMPINIT ." Space when ready "
2  TERMTEST JUMPSCAN ;
3 ;S
4 ( When JSCAN appears, the computer responds by asking for the
5  the CP/M file name under which the sets are to be stored,
6  the samples/mass level, the samples/second, the number of
7  scans, and the number and identity of the mass levels in
8  ascending order. Execution is stopped until a keystroke is
9  is entered. It then samples the mass levels given according
10 to the parameters entered and saves the data, and the
11 parameters, in IONCURR. The contents of IONCURR are saved
12 in the CP/M file name specified. The computer then halts
13 until a keystroke. If 0, the program ends. Anything else
14 causes the computer to repeat the above saving the new data
15 under a CP/M file name whose type has been incremented by 1. )

```

## SCR # 85

JDW 2/82 )

```

0 ( MOVION and READSCAN
1
2 45000 CONSTANT STATMEN
3 : MOVION IONCURR 10 + @ 200 - 2 /
4  IONCURR 200 + STATMEN MOVE ;
5
6 : READSCAN IONCURR 20 2 READIT
7  IONCURR DUP 10 + @ 2 READIT ;
8 ;S
9 ( MOVION causes the data in IONCURR to be moved to STATMEN.
10
11 When READSCAN appears, the computer will read a file whose
12 name is stored at UDN into memory location IONCURR. It
13 does this by first doing a partial read to gain access to
14 memory location IONCURR + 10. This tells the computer how
15 many bytes are in the file. )

```

## SCR # 86

JDW 2/82 )

```

0 ( HEADING, AVOUT and STAT1
1
2 : HEADING CR ." SET " 5 SPACES ." MASS " 5 SPACES
3  ." AVERAGE " 5 SPACES ." AVERAGE DEVIATION " CR ;
4
5 : AVOUT AV @ DUP 2DUP . 10 SPACES 4 1 DO I 10** < IF
6  SPACE ELSE ENDIF LOOP AD @ . ;
7 : STAT1 READSCAN MOVION IONCURR 8 + @ ;
8 ;S
9 ( HEADING is used in conjunction with the STAT routines to
10 provide a heading for data output.
11
12 AVOUT outputs the average and average deviation 14 spaces
13 apart left hand justified.
14
15 STAT1 reads a file to IONCURR and moves it to STATMEN. )

```

SCR # 87

```

0 ( STAT2                                JDW 3/82 )
1
2 : STAT2 IONCURR 4 + @ IONCURR @ * 0 DO
3   DUP DUP STATMEN SWAP I * 2 * +
4   KICKSORT LOOP
5   DUP IONCURR 4 + @
6   0 DO IONCURR
7   @ 0 DO 13 SPACES
8   DUP IONCURR 8 + @ 2 * DUP I * SWAP J * IONCURR
9   @ * + STATMEN + SWAP 2 - SWAP AVERAGE AVOUT
10  CR LOOP LOOP DROP ;
11 ;S
12 ( For a given set, STAT2 will determine the average and
13   average deviation of all the samples taken for a given
14   mass and a given scan and output these values.      )
15

```

SCR # 88

```

0 ( STAT3                                JDW 3/82 )
1
2 : STAT3 ." ALL SCANS " CR CR IONCURR @ 0 DO
3   MOVION IONCURR 4 + @ 0 DO DUP DUP
4   2 * DUP DUP J * SWAP I * IONCURR @ * + STATMEN +
5   SWAP I * STATMEN + MOVE
6   LOOP DUP IONCURR 4 + @ * STATMEN 2DUP
7   2DUP 2DUP HILODROP SWAP 2 - SWAP HILODROP
8   SWAP 4 - SWAP KICKSORT SWAP 4 - SWAP AVERAGE
9   IONCURR 20 + I 4 * + @ WRITE 9 SPACES AVOUT
10  CR LOOP 5 CR'S ;
11 ;S
12 ( STAT3 determines the average and average deviation for
13   all the scans and all the samples taken in a given set and
14   for a given mass level.      )
15

```

SCR # 89

```

0 ( JSTAT                                JDW 3/82 )
1
2 : JSTAT CR CR 6INIT 2INIT NUMSET @ 0 DO
3   CR ." SET " I 1+ WRITE CR
4   STAT1 STAT2 STAT3 DATANAM 8 + INCASCII
5   DROP LOOP ;
6 ;S
7 ( JSTAT is interactive and will ask for the run name and the
8   number of sets. It will then output the average and average
9   deviation for each scan for a given set and mass level and
10  output the average and average deviations for all the scans
11  and samples taken for a given set and mass level.      )
12
13
14
15

```

SCR # 90

```
0 ( HEADING2 and JSTAT1                                JDW 3/82 )
1
2 : HEADING2 CR ." SET " 13 SPACES ." AVERAGE " 5 SPACES
3  ." AVERAGE DEVIATION " ;
4
5 : JSTAT1 6INIT 2INIT CR CR HEADING2 CR CR NUMSET 0 DO
6  STAT1 I WRITE CR STAT2 DATANAM 8 + INCASCII
7  LOOP ;
8 ;S
9 ( HEADING2 provides a heading for JSTAT1.
10
11  JSTAT1 is used as a simplified form of JSTAT when only one
12  scan is taken in each set.
13
14
15
```

117

SCR # 95

```
0 51 LOAD ( UTILITIES )
1 52 LOAD ( UTILITIES )
2 53 LOAD ( UTILITIES )
3 54 LOAD ( READE )
4 55 LOAD ( 2SUM )
5 56 LOAD ( READIT )
6 57 LOAD ( SAVEIT )
7 58 LOAD ( AVERAGE )
8 59 LOAD ( KICKSORT )
9 60 LOAD ( HILODROP )
10 69 LOAD ( INITIALIZATION routines )
11 71 LOAD ( INTIME and TIMESET )
12 72 LOAD ( INCASCII )
13 73 LOAD ( SETHASS, TESTPORT and GETION )
14 74 LOAD ( CLRION and TERMTEST )
15 75 LOAD ( 1CAL )
```

SCR # 96

```
0 95 LOAD
1 76 LOAD ( 2CAL )
2 77 LOAD ( NORM and SMOOTH )
3 78 LOAD ( MAXIMUM )
4 79 LOAD ( CAL )
5 80 LOAD ( MASSARRAY )
6 81 LOAD ( SET AND PARSAVE )
7 82 LOAD ( JUMPINIT )
8 83 LOAD ( JUMPSCAN )
9 84 LOAD ( JSCAN )
10 85 LOAD ( MOVION )
11 86 LOAD ( HEADING, AVOUT and STAT1 )
12 87 LOAD ( STAT2 )
13 88 LOAD ( STAT3 )
14 89 LOAD ( JSTAT )
15 90 LOAD ( HEADING2 and JSTAT1 )
```

OK

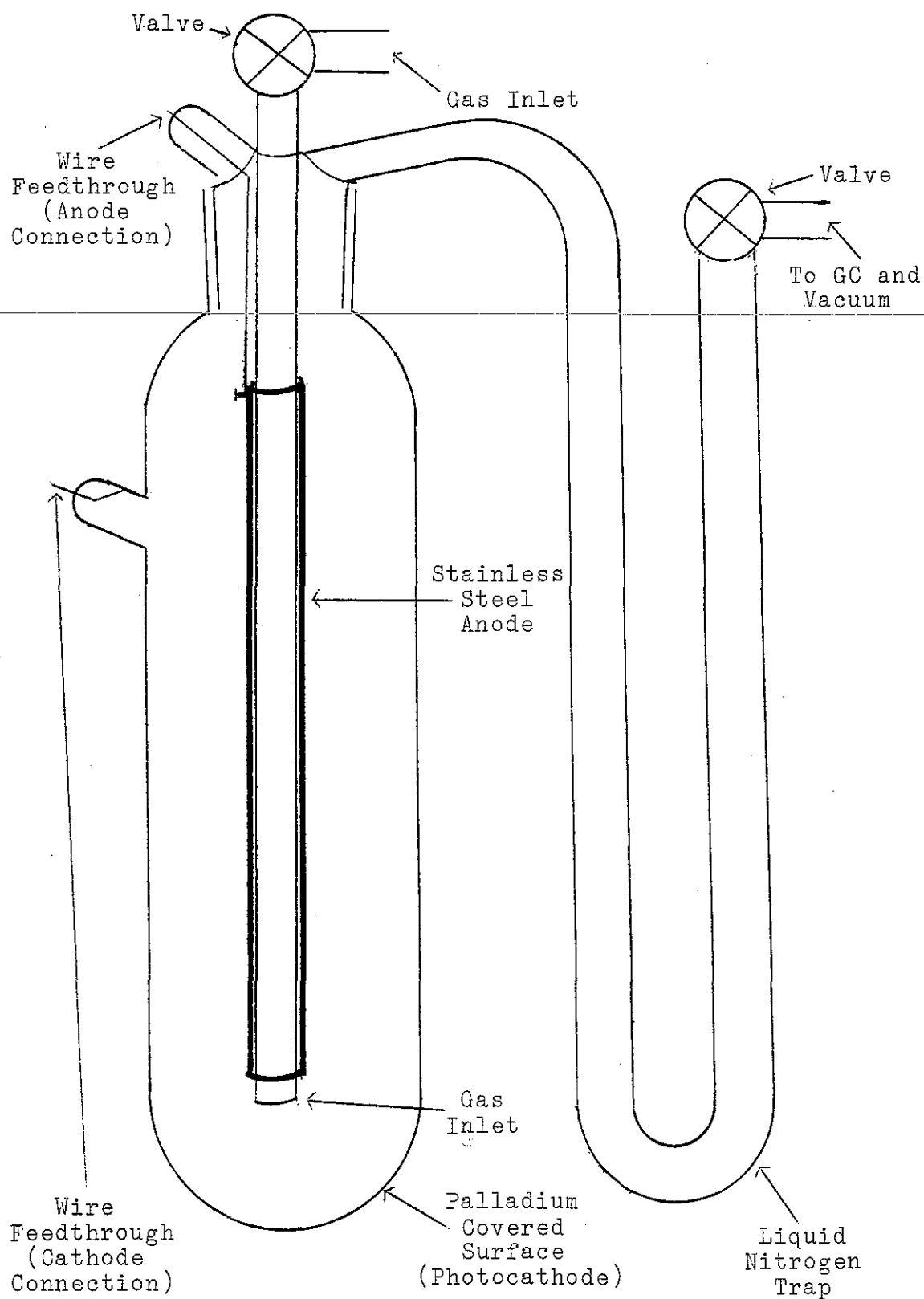
## APPENDIX F

### DEVELOPMENT OF PRESENT SYSTEM

The original goal of this research was to develop a system in which the chemical reactivity of gas phase molecules excited by low energy electron impact could be studied. Although this goal was not realized, the following summarizes the experiments conducted on the way to developing the system described in the experimental portion of this dissertation.

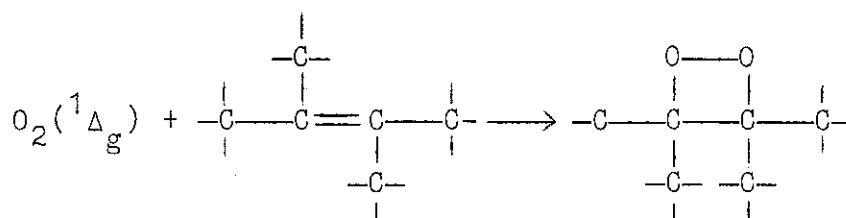
Figure F.1 illustrates the apparatus originally used in an attempt to excite gas phase molecules with low energy electrons. When the palladium surface is irradiated with ultraviolet light (General Electric Germicidal Lamp # FG 445-B), nearly monoenergetic electrons are emitted from the photocathodic surface. When a potential difference of 4.5 V is applied, a current of 0.6  $\mu$ A results. This is sufficient potential to excite dioxygen to the  $^1\Delta_g$  state. Experimentally, 2,3-dimethylbutene (DMB) was added to the reaction vessel until the current was suppressed to approximately 0.05  $\mu$ A. The vessel was then evacuated by freezing the DMB into the adjacent U-tube with liquid nitrogen causing the current to return to 0.6  $\mu$ A. Dioxygen was then added until the current was virtually zero. The two reactants were then mixed by sealing the vessel and allowing the DMB to thaw.

Figure F.1  
Static Reactor



The mixture was irradiated for 29 hours.

The reaction of  $O_2(^1\Delta_g)$  with olefins has been well studied in the literature.<sup>22</sup> However, very little work has been done in the gas phase. The reaction of  $O_2(^1\Delta_g)$  with DMB has been reported by Herron and Huie.<sup>23</sup> In their work,  $O_2(^1\Delta_g)$  was produced by passing  $O_2$  through a microwave discharge. The O atoms produced were removed by adding mercury vapor ahead of the reaction zone to form a thin mercury oxide film. DMB was then added downstream and the products were observed via mass spectrometry. A product with a mass of 116 amu was observed which was assumed to be the hydroperoxide:



It was hoped that the  $O_2$  and DMB in our system would react as well. However, the only mass increase noted occurred at 44 amu indicating the formation of carbon dioxide. This implies a combustion-like process. Water was probably produced, but the mass spectrometer was not set for that range. Acetone (another possible intermediate) was not observed.

There are several possible reasons for the failure to detect an intermediate. First, some ultraviolet light enters the vessel since the palladium surface is slightly transparent. Intermediates, such as the hydroperoxide, may

have entered into photocatalytic reactions. Second, the palladium surface may have catalyzed the combustion process. Third, there is always mercury vapor present in a vacuum system equipped with a Toepler pump. The light emitted from the mercury lamp was of the correct wavelength to excite mercury. Thus, the possibility of excited state mercury participating in the reaction cannot be ruled out.

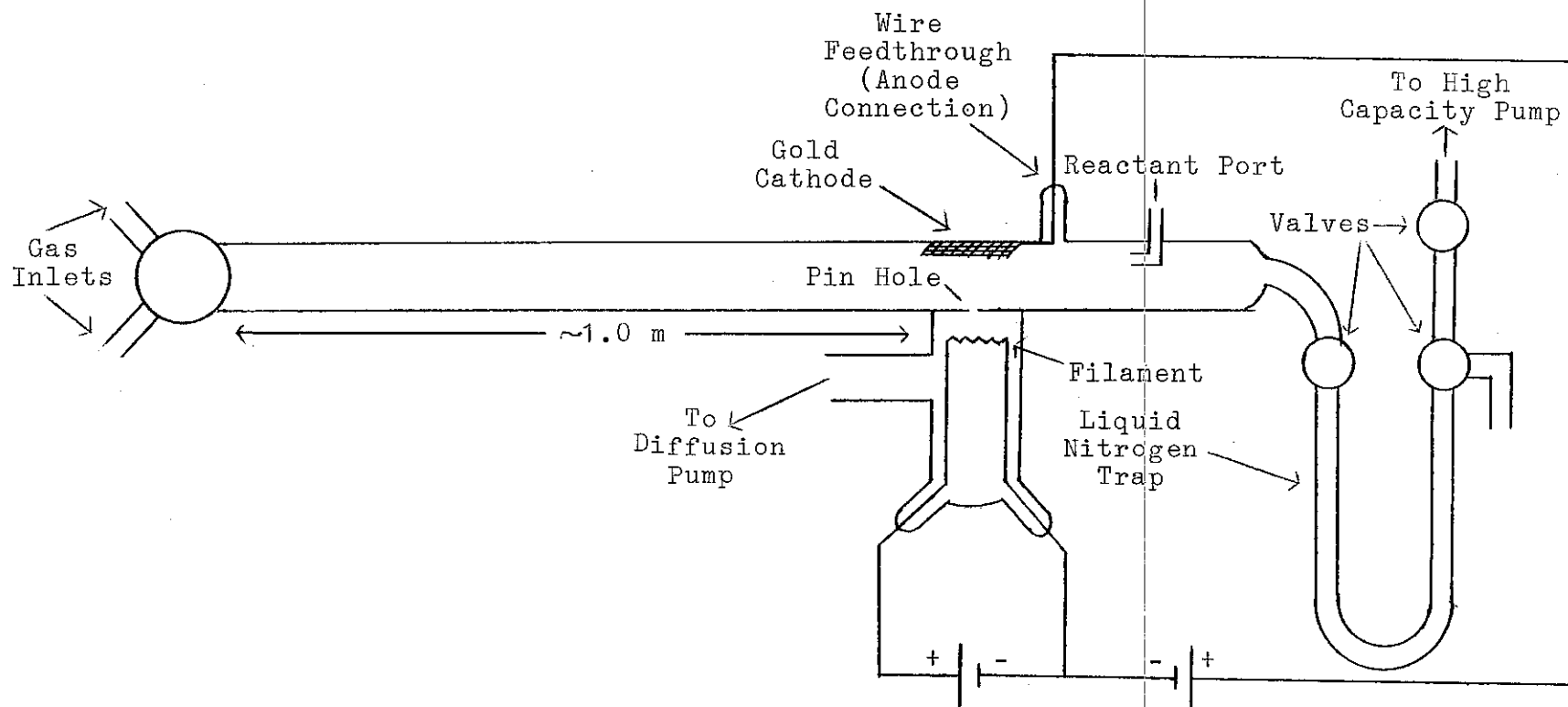
~~It was decided to change from the static reactor~~  
to a flow system in an attempt to overcome the above problems. Figure F.2 illustrates an early version of this attempt. Gas enters the 1 m tube and laminar flow is established before dioxygen reaches the activation sight. It was thought that laminar flow would keep oxygen molecules from being deactivated prematurely by collisions with the walls. A system like this requires much greater emission currents than are possible with a photocathodic surface emitter. A filament source was chosen. To prevent interaction with the hot filament, and to prevent disruption of laminar flow, the filament was isolated in a separate chamber that was evacuated with a mercury diffusion pump. The emitted electrons were to travel through the pinhole to the positive gold surface, exciting the oxygen molecules. The reactant would then be added 5 cm downstream and the products frozen out in the liquid nitrogen trap for subsequent GC/MS analysis. Unfortunately, we could never get the electron optics to work properly.

In retrospect, the reasons are obvious. First, the



Figure F.2

Early Flow Reactor



filament was of the wrong type. This will be discussed in more detail later. Second, the filament was placed too far from the gold surface.

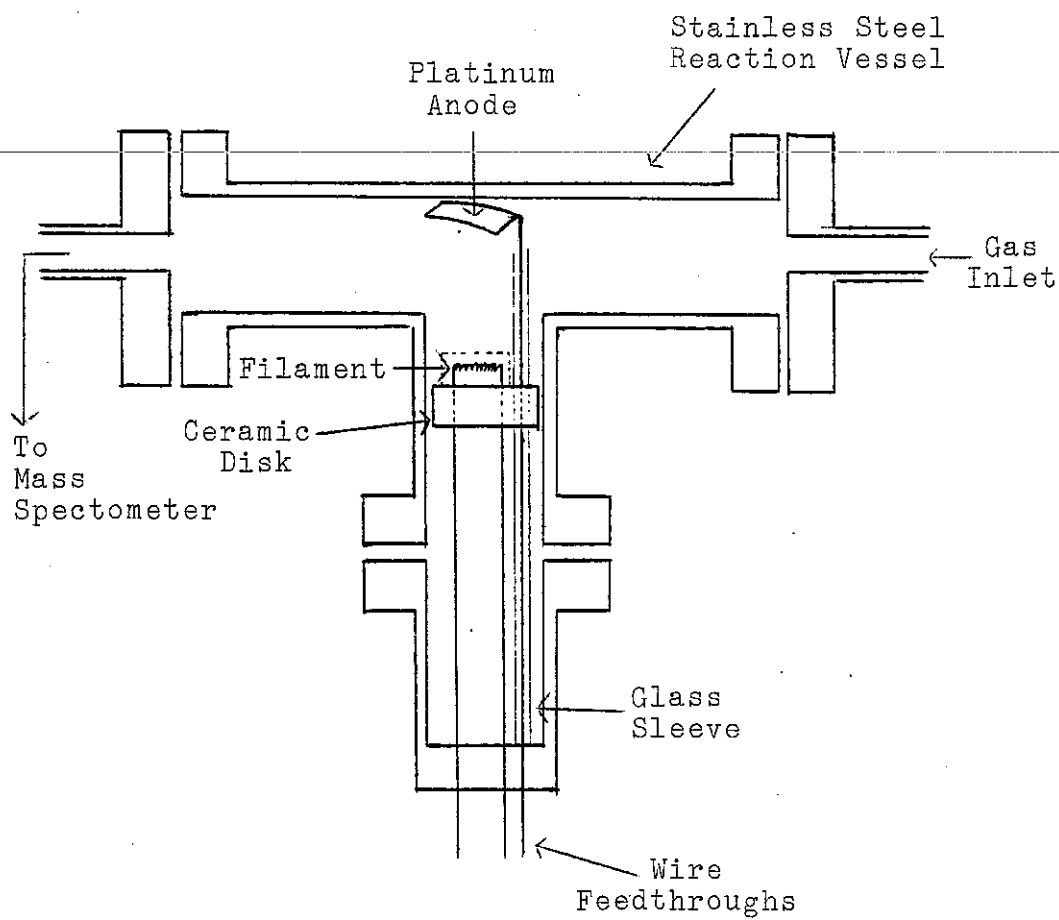
At this point, it was decided to forget about separating the product mixture via the GC and simply go to a flow system similar to what is presently in use. At the beginning, an attempt was made to isolate the filament from the flowing gases. This is illustrated in Figure F.3. This system did not allow the generation of an appreciable current, so we ultimately decided on the orientation shown in the experimental section.

A number of different types of filaments were tried in the apparatus shown in Figure F.3. The results of these experiments will now be summarized.

A tungsten filament from an automobile light bulb (GE part # W1158) was washed in 1,1,1-trichloroethane in an ultrasonic cleaner and dried at 110 °C for one hour. This was installed and generated 0.1 uA collector current at 0.6 A filament current. Pushing the filament current to 2 A gave an emission current greater than 1 mA. However, degassing was a serious problem and the filament burned out before the system was completely degassed.

Both rhodium and tungsten wire filaments (0.25 mm diameter) were tried but degassing was a problem. The coiled tungsten wire worked best with a collector current of 0.5 mA at 9 A filament current. Next, the tungsten wire was coated with a slurry of barium carbonate and current

Figure F.3

Precursor to Present  
Reaction Vessel

was passed through under vacuum to form a coating of barium oxide. This gave no improvement.

A filament from a General Electric 1258/93T high intensity 12 watt 12 volt light bulb yielded a collector current of 8.2 uA at 1.5 A filament current. Coating this type of filament with a slurry of barium carbonate and strontium carbonate helped. After the initial bakeoff, a collector current of 0.5 mA was obtained with very little degassing. However, the lifetime of the filament was very short.

It was at this point that the design of the apparatus was altered to the present form. Early experiments used a mass spectrometer filament wire (tungsten with 3% rhenium designed for use in the UTI 100B mass analyzer). At 2.1 A filament current and 1.00 V potential, the collector current was 0.08 mA. This filament was later found to be unacceptable since a retarding potential of 6.13 V was necessary to reduce the emission current to zero at 2.1 A filament current. However, some experimentation was done with this filament.

First, a mixture of  $O_2$  and DMB was passed through the reaction chamber. It was found that pyrolysis products were produced independent of potential difference. No exacting experiments were done since it was obvious that the mixture was simply interacting with the hot filament.

When  $N_2O$  was passed over the filament, the  $N_2O$  and O peaks decreased and the  $N_2$  peak increased with increasing

filament current. This was independent of potential and again represented interaction with the hot filament. It is suspected that O disappears because it forms an oxide with the hot filament.

A series of experiments were begun on forming gas which is approximately 40% H<sub>2</sub> and 60% N<sub>2</sub>. Although there were times when changes at masses 16, 30, 32 and 33 amu were thought to occur, nothing conclusive could be obtained. The experiments led to the isolation of the following problems:

1. The filament material operated at too high a temperature and electrons thus came off with too great a distribution of energies.
2. The channeltron electron multiplier was operating at 0.1% of its capability.
3. A large amount of low and high frequency noise is associated with the ion current reading.

The problems were solved concurrently before any further experiments were done. The filament material was replaced with a 1.0 cm thoria coated iridium wire filament as described in the experimental section. The second problem was solved by replacing the channeltron. This helped to solve the third problem. The third problem was further alleviated by using the dampening control on the control unit of the spectrometer to filter out high frequency noise and by using the microprocessor to filter out low frequency noise by computer averaging.

When all this was done, a definite change could be observed at 30 amu indicating the following reaction:



However, no pressure dependence was observed as would be

expected for a gas phase bimolecular reaction.

During this time, the procedures described in the experimental portion for detection of the effect of electron energy on the observed changes at a given mass level were developed. The pressure range of  $10^{-5}$  to  $10^{-4}$  torr was found to be convenient to work in.

When carbon monoxide was subjected to electron impact, ~~a definite pressure dependence could be observed at~~ 44 amu. Further investigation revealed changes at 16 and 30 amu as well. This was confusing until it was found that carbon suboxide (see the introduction), a product of the disproportionation of carbon monoxide, reacts with water to form methanol and formaldehyde. There is always water in the background spectra of our system. Adding an additional Vac Ion pump reduced the amount of water significantly.

It was at this point that interaction of carbon monoxide with the collector surface was suspected. This was tested by coating the surface of the collector with palladium and observing differences in the effect of low energy electron impact at 44 amu in the presence of carbon monoxide. The change at 44 amu was observed to be much more intense. There can now be little doubt that we were observing a surface effect from the beginning. The mean free path of CO at  $10^{-4}$  torr is approximately 0.5 m. This means that many collisions with the walls will occur, on the average, before a bimolecular event takes place. The chance for

deactivation of the excited state is high.

The above observations led to the experiments described and discussed in this dissertation.

---